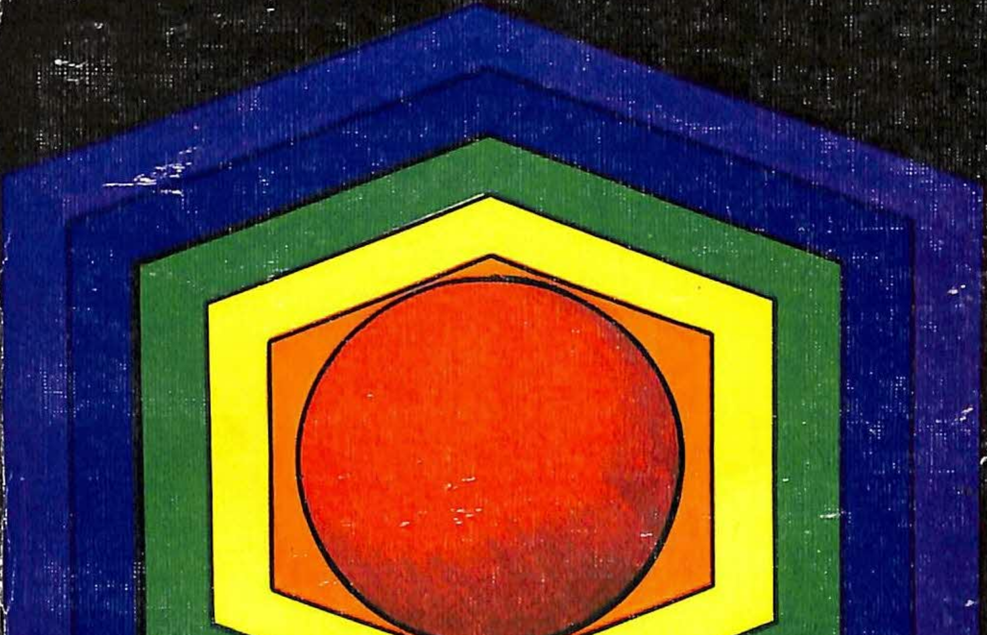
INORGANIC

CHEMISTRY

TEXTBOOK FOR SCHOOLS

Yu.V. Khodakov, D.A. Epshtein, P.A. Gloriozov

PART ONE



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INORGANIC

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Symbols

△	exercise
?	question
■	home assignment

1

First Notions of Chemistry

The Subject Matter of Chemistry

We begin studying chemistry. Together with physics and biology, chemistry is a natural science since it deals with nature. What is the subject matter of chemistry?

A minute grain is dropped into the soil in the spring. It begins growing and by the summer develops into a plant. Plants may be likened to natural 'factories' that turn raw materials such as carbon dioxide, water and other substances taken from the soil, into proteins, fats, starch, sugar and vitamins. Botany cannot explain how this complicated and mysterious work, the conversion of one substance into another can occur in the cells of plants. The explanation will be given by another science, chemistry.

Chemistry is the science of substances and their interconversions.

The plant and animal kingdoms give us food to maintain our lives. Not long ago, our clothes and footwear were also exclusively of natural origin: vegetable fibres, wool, the hair, and skin of animals. At the present time synthetic fibres and materials have in many cases replaced materials of plant and animal origin. Man has created materials that have never existed in nature. These man-made substances are produced at chemical plants from petroleum, coal, and natural gas.

The science of chemistry has taught man to produce these substances. The discovery of the laws by which one substance can be converted into another, allows man to predict and explain these interconversions of substances, to control them, and to utilize them for his own good. The better we know chemistry, the greater the possibilities that open up for man.

Chemistry now plays an important role in our daily life. It is true that we use food which is 'manufactured' for us by nature, but agriculture would never be able to give us all the food we need without the artificial fertilizers turned out by the chemical industry. The knowledge of chemistry has made it possible to use nuclear energy and conquer space.

Development of the chemical industry, and the complete utilization and incorporation in the economy of recent advances in modern chemistry will enable further development of national wealth, help manufacture better and cheaper capital and consumer goods.

We deal with chemistry in our everyday life. It penetrates our homes, and many non-chemical industries have become to a great extent dependent on chemistry. Conversion of one substance into another is always attended by liberation or consumption of heat, by emission and absorption of radiant and light energy, and by changes in the state of matter. Therefore, chemical research scientists use physical methods of investigation and physical theories. In turn, biological processes are closely related to transformations of substances in living organisms. Chemistry, chemical methods of study, and chemical theories greatly help biology and medicine in solution of their problems. Today the knowledge of chemistry is becoming more and more necessary in any branch of science and industry, and in any profession you may choose after you have graduated from school.

Now let us turn the first page in the fascinating book of CHEMISTRY.

1.1

Substance

Look around. Everything that surrounds us–living and inanimate nature, everything that has been made by man, even man himself–consists of substances. Physics defines the difference between the concepts of substance and object. Observe two different objects: a nail and a horseshoe. These are two different objects, but they are made of the same substance, iron. A piece of aluminium wire and an aluminium pan are different objects, but the substance is the same, aluminium.

Iron, aluminium, copper, water, sugar, oxygen, carbon dioxide, starch, proteins are all *substances*. More than three million substances are known to man by this time, and their number is still increasing. Some new substances are discovered in nature, while others, like nylon, are made by man himself. Each substance has been studied and given its name. (Three million substances give three million names, which by far exceeds the number of words contained in the most complete dictionary.) Substances may have much in common but still there will be a special feature that differs one particular substance from all others in the huge list of three million names. Each substance has its own properties and characteristics.

One of the aims of the science of chemistry is the description of substances. Each student must be able to describe a substance, i.e. to characterize its properties. Take table salt as an example. This is a colourless crystalline substance (white when crushed to fine powder) soluble in water, it is brittle, it tastes salty, it does not change when heated, etc. When describing a substance one should mention the properties that can be measured, e.g. boiling or melting point, density, etc. The effect that a substance has on man should also be indicated, since many substances are poisons. An unknown substance should therefore never be tested by taste. Some substances attack the skin, and they should not be handled directly.

Once the properties of substances are known, they may be utilized. Our ancestors knew that silicate rock is very hard and used it to manufacture their primitive tools and weapons.

A knowledge of the properties of substances is essential for their correct use. Articles made of nylon, for example, cannot be pressed with a hot iron, since this man-made substance has low melting point and easily melts.

A knowledge of the properties of substances is also necessary to identify and distinguish them from one another. A lump of an unknown mineral occasionally thrown into the fire, helped the discovery of an immense deposit of coal in the far North Arctic of the Soviet Union.

We shall learn from this book how man studied the properties of substances to discover their structure which cannot be determined by mere observation.

?
△

1. Write in two separate columns the names of substances and objects from the following: (a) a cup, oxygen, a key, an iceberg, mercury, a candle, water, iron; (b) lime, ceramic pipes, gypsum, roof tiles.
2. Describe the properties of (a) iron, (b) water, (c) coal, (d) carbon dioxide.

■

Describe (orally) the properties of sugar using the scheme given on p. 101. Test sugar for melting and combustibility in normal conditions by holding it in the flame of a match. Take precautions while using fire.

1.2 Pure Substances and Mixtures

When an object is studied, the question arises: what is it made of? Living organisms consist of organs, organs consist of tissues, and tissues of cells. So what are substances composed of? It is known from physics that substances cannot be divided to infinity. If water is poured into an open cup it will gradually disappear because *molecules* of water are separated from its surface and dissipated into the surrounding space. If a cold object is brought into a warm room, drops of water precipitate on its surface. These are formed by the condensation of water molecules contained in the air. The molecular principle explains this important property of water known as *volatility*. If water were not volatile, the continents would have turned into dry and lifeless deserts surrounded by oceans spread beneath an ever cloudless sky.

The smallest particle of water is a molecule of water, and the minutest particle of sugar is a molecule of sugar, etc.

Substances may have molecular and non-molecular structure. Gaseous and vaporous substances are all composed of molecules. This does not hold for crystalline substances. Crystals of quartz, granite, sand, etc., have no molecules. They are composed of *atoms* of silicon that are bound chemically with oxygen atoms. Many other substances existing in the form of large and fine crystals have non-molecular structure as well, e.g. common salt and soda, the substances very well known to everyone. They have no molecules.

All molecules of a given substance, for example of water, are alike. But they differ from molecules of other substances. This accounts for the different properties of various substances. Sugar is produced from various plants. We use it as lumps, fine grains, or powder, but it is still the same substance and

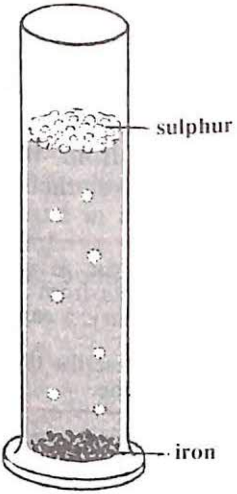


Fig. 1.1 Separating a mixture of iron and sulphur (*a*) in water

it has the same properties. If we dissolve equal weights of granular, powdered, or lump sugar in equal volumes of water, we shall obtain equally sweet solutions. Any substance will always have the same properties unless it contains impurities. Rain water will boil in any country at a temperature of 100°C and will freeze at 0°C (under normal atmospheric pressure of 760 mm Hg); the density of rain water will everywhere be 1 kg/litre at 4°C, and all other properties will be the same as well. At the same time, the properties of natural water taken from different rivers will vary and depend on the properties and amount of impurities that it contains.

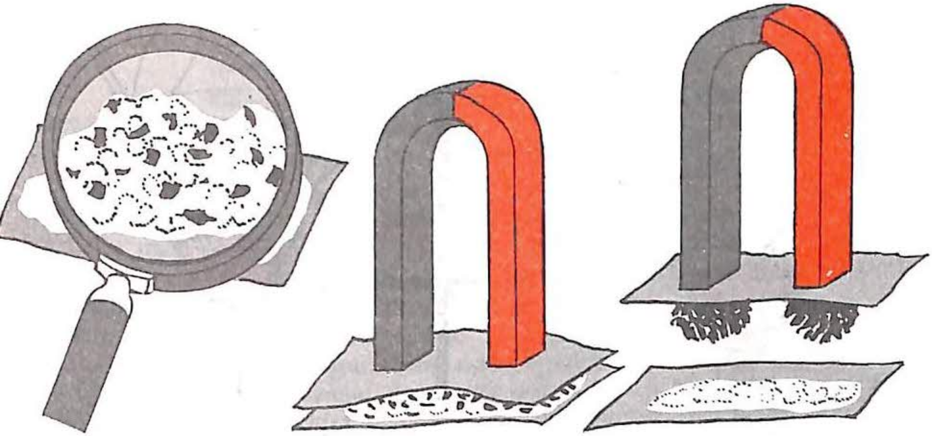
In practice we do not deal with pure substances because even the purest substance will contain this or that amount of impurities.

Modern science and technology, however, require substances in which impurities do not exceed a millionth fraction of one per cent. We call them ultrapure substances. Radio electronics and space research cannot do without ultrapure substances.

In chemistry 'substance' is understood to mean pure substance. But in everyday life we usually deal with mixtures rather than with pure substances. Air, for example, is a mixture of oxygen, nitrogen, carbon dioxide, and other gases.

When we shake powdered chalk in water, a milky liquid is obtained. This is a mixture of water with the chalk particles suspended in it. The naked eye can easily distinguish separate particles of chalk in the suspension. But it is not always easy to identify a mixture of substances by appearance. Milk, for example, seems to be a homogeneous substance but when viewed through a microscope it appears as a mixture of droplets of fat suspended in liquid.

Solutions form a special class of mixtures. When we shake sugar in water, a clear solution is obtained. It is impossible to observe sugar particles dissolved in water even if we use a microscope. But the presence of sugar in the liquid can easily be detected if we taste it, or if a drop of the solution is placed on a glass slide and allowed to dry: sugar crystals will remain on the glass.



and (*b*) by a magnet

When dissolved in water sugar is divided into molecules which are distributed evenly between the water molecules.

In order to study a substance and describe its properties it is first necessary to separate it from the mixture and remove impurities.

From everyday observations we know that the properties of separate substances are preserved in mixtures. This can be proved experimentally. Take two powders. One of them is grey and the other yellow. The grey powder sinks to the bottom when dropped into water, and it is attracted by a magnet (it hangs from its poles in garlands). The powder is crushed iron. The yellow powder is not attracted by the magnet and floats to the surface of water (it is not wetted by it). The yellow powder is sulphur. Mix the powders together. Take a pinch of the mixture and drop it into water. Shake it. Sulphur will float to the surface while iron will sink to the bottom (Fig. 1.1*a*). Now place the remaining mixture on a sheet of paper, cover with another sheet and apply the magnet to the surface of the upper paper: the iron and sulphur will separate – grains of iron will be attracted to the magnet (through the paper) while sulphur will remain on the lower sheet (Fig. 1.1*b*). Thus we have proved that the properties of individual substances (iron and sulphur) have not altered after they were mixed together: sulphur remained unwettable and iron was attracted by the magnet. These properties of sulphur and iron were utilized in our experiment to separate the two substances.

?
△

1. Which of the following properties (shape, boiling point, particle size, weight) can, which cannot, be specified in the description of (a) a substance and (b) a molecule?
2. You know that substances can be separated by settling, filtration (Fig. 1.2), and evaporation. Give examples of the separation of substances by each of these methods.
3. What differences in the properties of milk components are used for the separation of cream by settling?

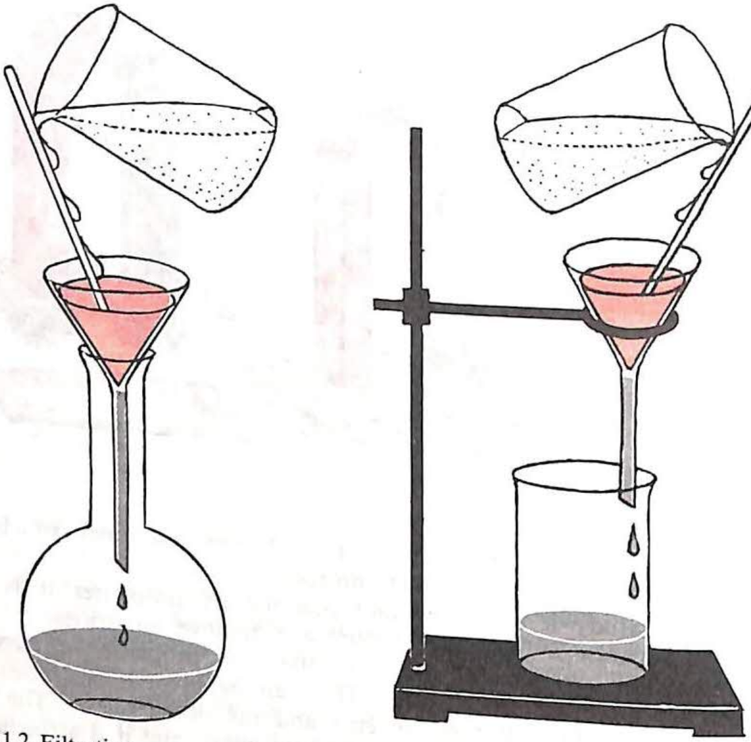


Fig. 1.2 Filtration

4. Explain why rain water has the same properties in all countries while water taken from various rivers differs in its properties?
5. Why can we not say 'a molecule of granite', 'a molecule of milk', 'a molecule of air'?
6. What is a solution of sugar from the viewpoint of the theory of molecules?
7. Write in separate columns the names of substances and of mixtures of substances among the following: sugar, sea water, soil, oxygen, air, milk, aluminium, granite.
8. What materials are used for the manufacture of filters?
9. Can sugar be separated from its solution by filtration? Reason your answer.
10. Observe Fig. 1.2 and describe the method by which a mixture of saw dust may be separated from water.

■ Prove the presence of dissolved solids in potable water.

1.3 Physical Phenomena

Everything around us, all living organisms, mineral matter, and man himself undergo incessant changes. All substances likewise undergo various changes. These are known as *phenomena.* A substance can be ground to powder, it can be melted, dissolved, or recovered from solution. The substance will remain the same substance.

A lump of sugar may be crushed to powder in a mortar and its minutest particles may be carried by air like dust if we gently blow. A particle of finely powdered sugar can only be seen in a microscope. But sugar can be disintegrated into even smaller particles using neither hammer nor mortar: we can do this by dissolving sugar in water. If we remove water from a solution of sugar by evaporation, sugar molecules will combine back into crystals. Sugar remains sugar no matter whether it is crushed or dissolved.

When evaporated, water is converted into its gaseous state known as steam. When cooled, water turns into ice, which is the solid state of water. The minutest particles of water are molecules of water. The minutest particles of ice or steam are also water molecules. Liquid water, ice, and steam are not different substances. They are one and the same substance known as water in its different *states of aggregation.*

Like water, many other substances can also be converted from one state of aggregation into another. Any metal can be melted, i.e. converted into its liquid state, and turned into gas. In the outer envelope of the Sun, where the temperature is about 6000°C, iron and other metals are found in the gaseous state. Conversely, a gaseous substance, for example carbon dioxide can be turned into a solid (dry ice) by cooling.* No new substances are formed by all these phenomena.

Events in which substances are not converted into new substances are called physical phenomena.

?
△

1. May the following be defined as physical phenomena: (a) formation of clouds, (b) filtration, (c) crystallization, (d) evaporation? Reason your answer.
2. What physical phenomena have you observed (a) in your house, (b) at school, (c) in nature?
3. How will you separate a mixture of river sand and table salt? Plan your experiment and describe the phenomena that will occur at each stage in the procedure.
4. How can the following mixtures be separated into their components: (a) iron and copper shavings, (b) chalk and sugar, (c) vegetable oil and water, (d) a solution of table salt in water? Describe the properties of each particular substance that will be used for its separation from the mixture.
5. Sometimes substances are purified by crystallization: the substance is dissolved, the solution evaporated, and the damp crystals are dried in blotting (filter) paper. Explain.

---

* Normally, when we describe a substance as a gas, solid, or liquid, we mean its state under normal conditions.

1.4

Chemical Phenomena

Let us now consider some phenomena that differ substantially from physical phenomena.

Iron rusts in damp air. It partly converts into a red-brown powder known as rust, which is a substance quite different from iron.

A copper plate, when heated in the air, loses its lustre and becomes covered with a black coat, that can easily be removed by scraping (Fig. 1.3). If we continue heating copper, periodically scraping off the black coat, we can convert all the copper into a black powder, copper scale or oxide. This is a new substance having new properties: when we cool copper oxide it does not turn back into copper.

A ribbon of magnesium burns in air to emit bright light (Fig. 1.4) and to turn into magnesium oxide, a new (white) substance.

If we take a glass tube and blow air through a solution of lime (lime water), the liquid becomes clouded by a white chalk-like powder which is formed in solution. The powder precipitates gradually to the bottom. This is a new substance formed by the lime dissolved in water and the carbon dioxide exhaled from our lungs.

Place granulated sugar in a test tube and hold it over the flame of a burner (Fig. 1.5). Sugar first melts (a physical phenomenon), and then turns brown. A pungent odour can be smelt and vapour is expelled from the melt. The vapour is condensed on the cold walls of the test tube in the form of drops. This is the water that is contained in sugar although it appears to us to be a dry substance. At the end of the experiment sugar is charred into a black substance which is devoid of taste; it does not melt, nor does it dissolve in water. This is coal. The sugar has decomposed into new

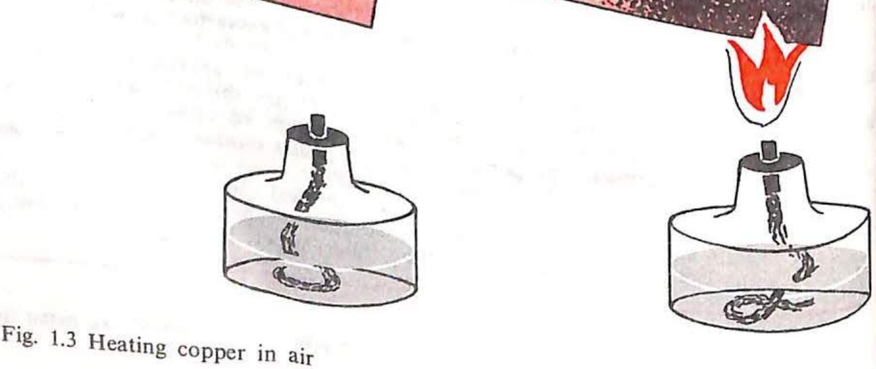


Fig. 1.3 Heating copper in air

Fig. 1.4 Burning a magnesium ribbon

substances among them water and carbon which do not resemble the initial sugar in their appearance.

When a log of wood burns, it seems that its component parts disappear leaving no trace. But let us introduce a burning match into an upturned glass cup: the inner walls of glass become covered with droplets of water. Rinse the cup with lime water, cover it with a glass slide and shake it: the droplets of lime water become cloudy. We already know that carbon dioxide can turn lime water cloudy. We can thus conclude that wood burns to form carbon dioxide and water, entirely new substances that are unlike wood itself.

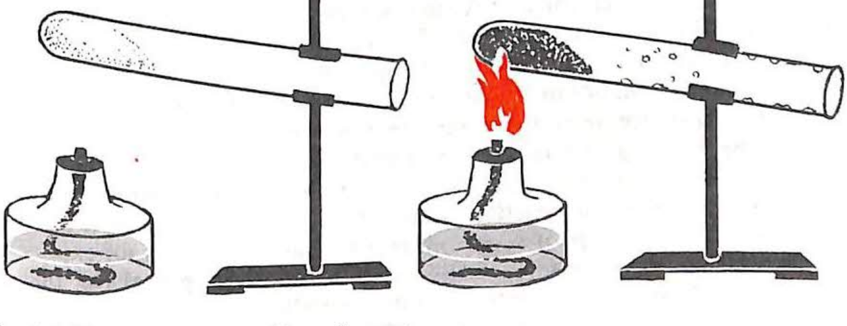


Fig. 1.5 Thermal decomposition of sugar

What is common to the described phenomena?

New substances are formed from the initial compounds in all the described phenomena and they can all be classified as chemical phenomena. **Chemical phenomena are those by which one substance is converted into another. These are known as chemical reactions.**

What is the difference between chemical and physical phenomena from the molecular viewpoint?

Molecules of a substance remain unchanged in physical phenomena, while in chemical reactions they are transformed into molecules of other substances.

? △

1. Describe the chemical reactions of: (a) carbon dioxide with lime water, (b) wood burning, (c) sugar decomposition, (d) copper heating in air.
2. Which of the following phenomena are chemical and why: (a) metal forging, (b) food burning in an overheated saucepan, (c) formation of a sugar crust on the surface of drying jam, (d) coagulation of milk, (e) putrefaction of an egg, (f) formation of snow flakes, (g) evaporation of alcohol, and (h) burning of alcohol.

1.5

Signs and Conditions of Chemical Reactions

What are the apparent signs of a chemical reaction that can differentiate it from a physical phenomenon? Some substances disappear and others are formed in a chemical reaction. The disappearance of the initial substances and formation of reaction products are the signs by which we can conclude that a chemical reaction has occurred.

When a copper plate is heated its colour changes. As carbon dioxide is blown through lime water, a white substance precipitates. When wood burns, droplets of water precipitate on the cold walls of the vessel. Burning magnes- m turns into a white powder with liberation of heat, and emits light and diant energy.

Change in colour or odour, formation of a precipitate, evolution of gas or nergy—all these are signs of a chemical reaction.

When we study a chemical reaction we pay attention not only to the manner in which it occurs, but also to the conditions under which a chemical reaction is initiated and completed.

What are the conditions required for a chemical reaction to begin?

In the first instance, in order to initiate a chemical reaction it is necessary to bring the reacting substances (*reactants*) into contact. The smaller the particle size of the reactants, the more close the contact ensured between them, and the sooner the reaction occurs. It is difficult to ignite a lump of sugar, while a fine powder of sugar burns instantaneously with an explosion. (Sometimes sugar dust spontaneously explodes at sugar processing plants.)

Crushing of substances into minute particles can be attained by dissolution. Preliminary dissolution of the initial substances will therefore significantly facilitate a chemical reaction between the reactants. Reactions between solutions are therefore used wherever possible.

Contact between the reactants will be enough in some cases to initiate a chemical reaction (as in the case of damp air and iron), while in other cases contact alone will be insufficient. For example, copper does not react with the oxygen of the air at 20-25°C. In order to achieve a reaction between copper and oxygen we have to heat the metal.

Heating varies in its effect on the initiation and course of chemical reactions. Some reactants need continuous heating in order to complete a chemical reaction, and when the source of heat is removed, the chemical reaction is suspended. Thermal decomposition of sugar is a typical example.

In other cases heat is only required to initiate a chemical reaction which will continue spontaneously when the source of heat is removed. Examples of such reactions are the burning of magnesium, wood, and other combustible substances.

?
△

1. What are the signs of the following reactions: (a) rusting of iron, (b) burning of a candle, (c) decomposition of sugar?
2. Name the conditions that favour the initiation and rapid course of a chemical reaction.
3. Give examples of reactions that are only initiated by heating and can continue spontaneously when the source of heat is removed.
4. How can a lump of sugar be divided into molecules? How can a molecule of sugar be destroyed?

1.6

Chemical Reactions Around Us

Look around. Most objects that surround us, such as concrete buildings, household utensils, etc., have not been made from materials that are found in nature ready for use, but have been manufactured by man with the use of chemical reactions. Chemical reactions occur everywhere. They occur inside ourselves.

Energy liberated in chemical reactions is widely used in everyday life, at home, in industry, in launching of space crafts. "Widely has chemistry spread its arms in human life. Wherever we cast a glance, we find fields of its application," said the great Russian scientist M. Lomonosov.

Long ago, our forefathers acquainted themselves with chemical phenomena. This happened long before man created a science known as chemistry: our ancestors of distant times learned how to handle fire (the combustion reaction) and this saved them from cold during the Ice Age.

Time passed on, and man learnt how to melt metal from ores. Stone tools and weapons were then replaced by better metal ones. The invention of gun powder helped townspeople to overthrow the rule of the feudal nobility.

The mystery of the chemical reactions was used by priests beginning from ancient Egypt to keep the common people in religious servitude.

Science has dispelled these mysteries and taught people how to use chemical reactions for their own good.

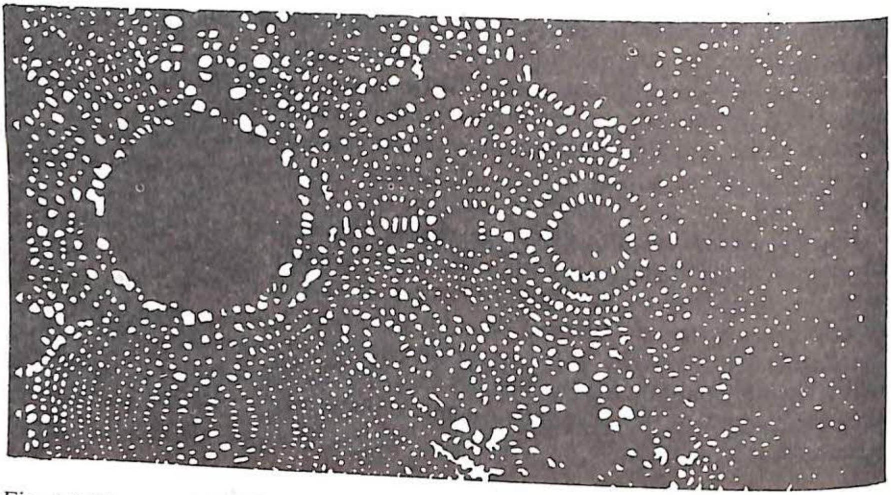


Fig. 1.6 The surface of a sharp point of a tungsten filament (the image is distorted like in a bad mirror)

1.7 The Atom

A chemical reaction consists in the conversion of certain substances into others. Molecules of all substances consist of even smaller particles known as *atoms*.

The invention of the microscope made it possible to observe a microbe. Since then the magnifying power of modern instruments has increased immensely compared to the microscope and molecules and atoms can now be photographed. In these photographs (Fig. 1.6) atoms appear as specks of light and molecules as combinations of such specks.

The number of atom types is limited. Atoms of one type are alike, but they differ from atoms of all other types.

Atoms combine with one another in different ways. Like the letters of the alphabet that can be combined to form hundreds of thousands of different words, the same atoms can combine to form molecules of different substances. For example, atoms of only two kinds, oxygen and hydrogen can form several substances, such as hydrogen, oxygen, and water (see Fig. 1.7).

A molecule of water consists of three interconnected particles, atoms. An oxygen atom (designated by the letter O) combines with two hydrogen atoms (letter H). A molecule of oxygen is composed of two oxygen atoms, and a hydrogen molecule of two hydrogen atoms.

Unlike oxygen atoms, metal atoms in the gaseous state do not combine in molecules. These are *monatomic* molecules. The atom of copper can therefore be considered as the molecule of copper and the iron atom as the iron molecule, etc.

What happens to molecules and atoms of substances during a chemical

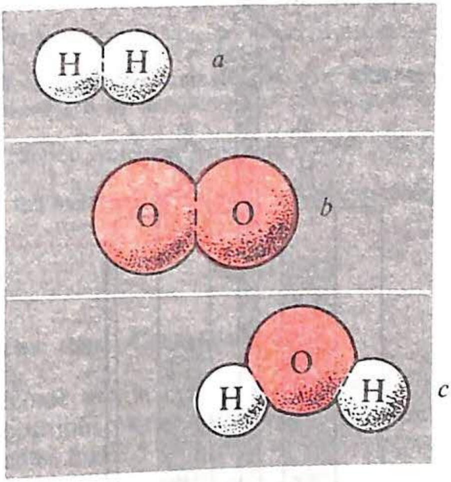


Fig. 1.7 Diagram of molecules of (*a*) hydrogen; (*b*) oxygen; (*c*) water

reaction? To answer this question let us consider in detail the reaction of water decomposition.

Water is a stable substance. It only decomposes at very high temperatures or when an electric current is passed through it. The decomposition of water is accompanied by the liberation of gas bubbles. If the gas is collected and studied we can establish that this is a mixture of two gases. The gases can be separately collected. To do this immerse two metal plates in water and connect them to the source of direct electric current. As gases are evolved, collect them in separate test tubes held over each plate (Fig. 1.8). The volume of gas collected in one test tube will be twice as large as the other. Put a burning splint to the mouth of the test tube containing the larger volume of gas: it burns. This is combustible gas, hydrogen. Put a glowing splint into the test tube containing the smaller amount of gas: the splint burns energetically. The gas is oxygen. The decomposition of water into hydrogen and oxygen can be shown by the following diagram

$$\boxed{\text{water}} = \boxed{\text{hydrogen}} + \boxed{\text{oxygen}}$$

What happens to the molecules of water during their decomposition? The reaction can be represented schematically as in Fig. 1.9. Each water molecule divides into two hydrogen atoms and one oxygen atom. Two molecules of water give two oxygen atoms and four hydrogen atoms (i.e. twice as much). The like atoms combine in pairs to form molecules of new substances, viz. molecules of oxygen and hydrogen. Molecules of a substance are thus destroyed by a chemical reaction, whereas atoms remain unchanged.

Chemical reactions consist in the formation of new substances from the atoms contained in the initial substances.

Thus, *the atom is the chemically indivisible particle of a substance.* (In Greek *atomos* means uncut or indivisible.)

1.7 The Atom

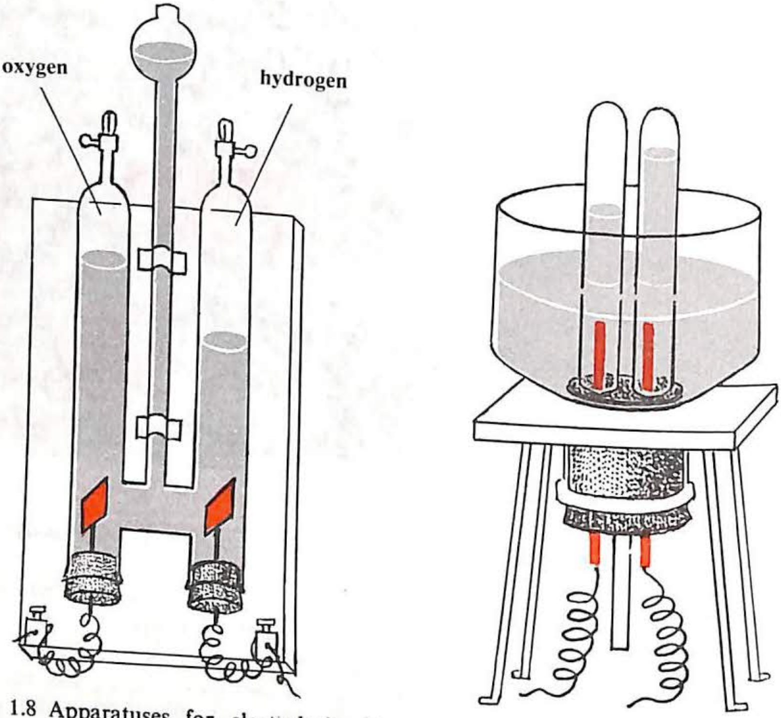


Fig. 1.8 Apparatuses for electrolysis of water

But there exist phenomena in which an atom can be further divided to turn into an atom of another type. Man can now create atoms that have not yet been found in nature. This is however the subject matter of another science known as nuclear physics.

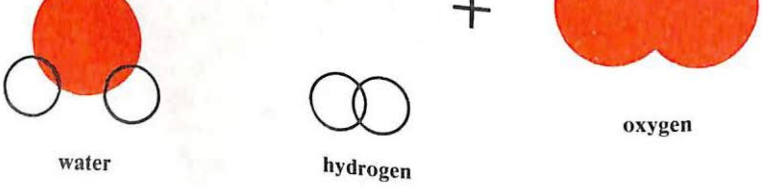


Fig. 1.9 Schematic diagram of water decomposition

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1. What is an atom? Why can we not say, 'an atom of water' or 'an atom of sugar'?
2. Which three types of atoms are contained in sugar? (Remember what substances were discovered by us among the products of sugar decomposition.)
3. What is a chemical reaction from the viewpoint of the science of atoms?
4. How can we explain the existence of so many substances around us?

1.8

Simple Substances and Compounds

We have already become acquainted with substances that differ in their composition. Some of them, e.g. gaseous oxygen or hydrogen, consist of molecules formed by atoms of one type only. Hydrogen and oxygen are thus simple substances. Others, for example water, are composed of atoms of various types. These are known as *compounds*.

Substances consisting of atoms of one kind are called simple substances.

Substances composed of atoms of various types are compounds.

Apart from hydrogen and oxygen we can name many other simple substances such as graphite, sulphur, and all metals (iron, copper, magnesium, etc.). Graphite is composed of atoms of one type, known as carbon atoms; iron consists only of iron atoms; copper of copper atoms, etc.

The difference between mixtures and compounds should be clearly understood.

Consider powdered sulphur and iron. In our experiment we mixed them to form a mixture of two substances in which sulphur and iron retained their individual properties and did not form any new compounds.

Now prepare a mixture of the same substances taking 4 g of sulphur and 7 g of iron. Place the mixture in a test tube and heat slightly over a burner (Fig. 1.10). When the mixture begins to redden, remove the burner and observe: the mixture will continue reacting and will soon become red hot. This indicates that a chemical reaction occurs between iron and sulphur with the evolution of heat. Cool the test tube, break the contents, grind them in a mortar, and examine. We shall distinguish neither sulphur nor iron particles. The product of the reaction is a black homogeneous powder. Hold a magnet over the powder: no iron particles are attracted to it. When dropped in water, the powder also fails to be separated into iron and sulphur. The black powder differs from both iron and sulphur in its density, melting point, and in all other properties.

Iron and sulphur combine together to form an entirely new substance, iron sulphide. Conventionally this reaction can be shown as follows:

iron + sulphur = iron sulphide

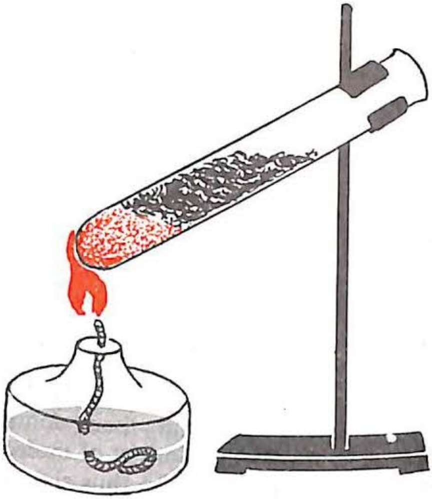

Fig. 1.10 Addition reaction between iron and sulphur

Iron and sulphur are simple substances. Iron consists of iron atoms and sulphur of sulphur atoms while iron sulphide is a compound that consists of both iron and sulphur atoms. If we designate the atoms of iron and sulphur by circles, we can represent the same reaction as shown in Fig. 1.11. Crystals of iron and sulphur are split into atoms, and the atoms of iron and sulphur combine into crystals of iron sulphide. There are no separate molecules in the crystals of such substances (Fig. 1.11), the entire crystal being one gigantic molecule. It would therefore be wrong to say that iron sulphide, table salt and like substances consist of molecules in the solid state. Their structure is non-molecular.

The mixture of iron and sulphur differs from iron sulphide in the following respects: (1) iron and sulphur preserve their individual properties in a mixture, while they do not have these properties in iron sulphide; (2) iron and sulphur can be separated from their mixture by physical methods, while

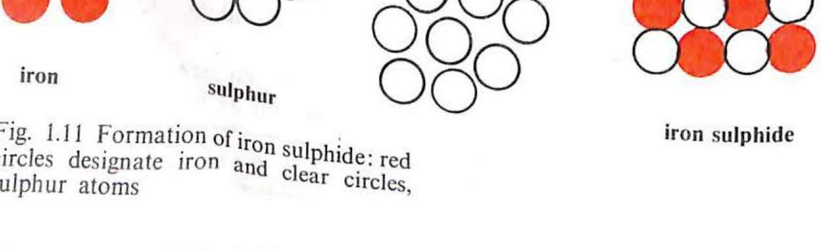

Fig. 1.11 Formation of iron sulphide: red circles designate iron and clear circles, sulphur atoms

this is impossible with sulphur and iron combined in a compound. Any mixture differs from a compound in that the properties of the individual components of the mixture are not altered.

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1. A molecule of carbon dioxide contains one atom of carbon and some oxygen atoms. Is carbon dioxide a mixture or a compound?
2. What is the difference between steam and a mixture of hydrogen with oxygen?
3. Describe the reaction between iron and sulphur and explain it from the aspect of atomic science.

1.9

Chemical Elements

Element is another word that chemistry borrowed from the ancient thinkers, who believed that the physical universe was composed of four simple substances: fire, air, water, and earth.

The chemical element means the same as a *type of atoms.* Oxygen atoms are the atoms of one type, or of one element called oxygen; the atoms of mercury are atoms of another type, of the element known as mercury, etc. At the present time 107 types of atoms, or 107 chemical elements are known. Most of them are found throughout the universe, making up the most remote stars and nebulae.

A chemical element should be differentiated from the notion of 'simple substance'. We discovered carbon among the products of decomposition of sugar. Hence we can conclude that carbon atoms are a component part of sugar. But it would be wrong to think that a colourless water-soluble substance sugar contains the black insoluble substance coal. Carbon atoms, before they combine to form coal, have first to break their bonds with atoms of other elements. This has happened in our experiment with the thermal decomposition of sugar. The same happens to food if we leave it on the stove and forget to turn gas off in time.

Carbon and coal differ. Carbon is a definite type of atoms, in other words it is a chemical element. The atoms of the element carbon may form part of various compounds and may be isolated in the free state. Carbon atoms combine with each other to form the simple substance which we know as coal.

In this particular case the chemical element (carbon) and the corresponding simple substance (coal) have different names, but most elements are given the same name as the corresponding simple substance. The words 'oxygen', 'iron', etc., may therefore mean both the chemical element and the simple substance. We must learn to distinguish between them. When we say 'man breathes oxygen' or 'oxygen is a gas', we mean the simple substance called oxygen (in other words we mean the molecules of oxygen). But when we say 'oxygen is contained in mercury oxide' we mean the chemical element oxygen (oxygen atoms). When we say 'a magnet attracts iron', or 'nails are made from iron' we mean iron as a simple substance, whereas in the sentence 'iron is a component part of rust' we mean the chemical element iron.

All chemical elements are divided into two major groups: metals and nonmetals. The atoms of metals combine with one another to form simple substances. Metals, as simple substances, have many properties in common. They are nontransparent, have a metallic lustre, and readily conduct electricity and heat; they are also malleable and can be forged into different shapes (unlike, for example, glass which is brittle and falls into pieces when struck). The group of metals includes iron, copper, aluminium, mercury, gold, silver, etc. The other group of chemical elements are nonmetals. The group includes carbon, oxygen, hydrogen, sulphur, etc. The atoms of nonmetals also combine with one another to form simple substances. But unlike metals their simple substances do not have very much in common. Their common characteristic is the absence of metal properties, i.e., they have no metallic lustre, and are poor conductors of electricity and heat.

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1. What is a chemical element?
2. Into what two major groups are all chemical elements divided? What are the differences in the appearance and basic properties of their simple substances?
3. What elements make up (a) water, and (b) sugar?
4. Write down the following sentences in your note-book and underline the word 'oxygen' where a chemical element is meant: (a) pure water contains oxygen; (b) tap water contains dissolved oxygen; (c) water is decomposed to liberate oxygen and hydrogen; (d) fish do not breathe the oxygen that is a component part of water, but the oxygen dissolved in water.
5. Write down definitions of simple substances and compounds, using the notion of a 'chemical element'.

1.10 Symbols

Chemistry uses its own language of symbols by which the composition of substances and the reactions occurring between them are described.

Each chemical element is given its own symbol, which is the initial letter of the name or its first letter and one of those which follow. Hydrogen, for example, is designated by the letter H, oxygen by O, etc.

The symbol H is used to designate both the element hydrogen and one atom of hydrogen. The letter O means the element oxygen and one oxygen atom; the letter C, the chemical element carbon and a carbon atom, etc. (see Table 1.1).

Some elements are designated by letters that do not coincide with the initial letters of their English names, e.g. the symbol of silver is Ag (stands for Latin argentum), and of mercury is Hg (Latin hydrargyrum), etc.

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1. Remember the symbols of the elements given in Table 1.1.
2. Which of the tabulated elements are known to you as existing in the free state?

Table 1.1

Names, Symbols, and Atomic Weights of Some Chemical Elements

Name of chemical element	Symbol	Atomic weight (rounded)	Name of chemical element	Symbol	Atomic weight (rounded)
Aluminium	Al	27	*Mercury*	Hg	201
Carbon	C	12	Nitrogen	N	14
Copper	Cu	64	Oxygen	O	16
Hydrogen	H	1	Phosphorus	P	31
Iron	Fe	56	Sulphur	S	32

Note. The other chemical elements will be given in Table II.1 on page 115 further in the text.

1.11 Atomic Mass (Weight)

However small the size of an atom may be, the weight of each chemical element has been determined. If we were to express the weight of atoms in the mass units that we normally use in everyday life (kilograms or pounds), the way of writing them would be very inconvenient. For example, the weight of a carbon atom is

$$m_a(\mathrm{C}) = 0.000\,000\,000\,000\,000\,000\,000\,02\ \mathrm{g} = 2.0 \times 10^{-23}\ \mathrm{g} = \\ = 2.0 \times 10^{-26}\ \mathrm{kg}$$

while the weight of oxygen atom is

$$m_a(\mathrm{O}) = 2.66 \times 10^{-23}\ \mathrm{g} = 2.66 \times 10^{-26}\ \mathrm{kg}$$

It would be difficult to remember these figures, or to perform calculations. Scientists have therefore developed a special system to express the weight of different atoms. They assumed a special unit, known as atomic mass unit (amu), which is 1/12 the weight of a carbon atom, while the weights of all other chemical elements are compared to this relative weight unit. One atomic mass unit measures 1.66×10^{-24} g. Atomic weights of all chemical elements can thus be expressed by whole numbers, which are actually their *relative* weights. The relative weight of an oxygen atom, for example, is

$$\frac{2.66 \times 10^{-23}\ \mathrm{g}}{0.166 \times 10^{-23}\ \mathrm{g}} = 16$$

Atomic weights of all other chemical elements can be calculated similarly.

The relative atomic weight of an element is the ratio of its atomic weight to 1/12 the weight of carbon atom.

It is denoted by A_r. The atomic weight is a dimensionless quantity, which should be differentiated from the weights of atoms expressed in atomic mass units (amu).

The mass of atoms is determined as the product of the relative weight of the element and 1 amu. For example,

$$m_a(\mathrm{O}) = 16 \times 1 \text{ amu} = 16 \text{ amu}$$

Compare:

$$m_a(\mathrm{C}) = 12 \text{ amu}; \qquad A_r(\mathrm{C}) = 12$$
$$m_a(\mathrm{S}) = 32 \text{ amu}; \qquad A_r(\mathrm{S}) = 32$$
$$m_a(\mathrm{H}) = 1 \text{ amu}; \qquad A_r(\mathrm{H}) = 1$$
$$m_a(\mathrm{Fe}) = 56 \text{ amu}; \qquad A_r(\mathrm{Fe}) = 56$$

Relative atomic weights of some elements are given in Table 1.1.

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1. What is the difference between a relative atomic weight of an element and the mass of its atom?
2. How does the mass of the magnesium atom compare with the mass of a carbon atom?
3. Which of the following figures: 10 amu, 30 amu, 36 amu, 48 amu can designate the atomic weights of carbon and magnesium?
4. Calculate the relative atomic weight of hydrogen if the mass of the hydrogen atom is
$m(\mathrm{H}) = 0.000\,000\,000\,000\,000\,000\,000\,00166 \text{ g} = 1.66 \times 10^{-24} \text{ g}$

1.12

Constant Composition

To prepare iron sulphide we have to mix together 4 g of sulphur and 7 g of iron. Why can we not take, for example, 9 g of iron?

One atom of iron combines in iron sulphide with one atom of sulphur. This means that regardless of the total weight of iron sulphide, it will be composed of equal numbers of sulphur and iron atoms:

$$m_a(\mathrm{Fe}) : m_a(\mathrm{S}) = 56 \text{ amu} : 32 \text{ amu} = 56 \text{ g} : 32 \text{ g} = 7 : 4,$$
$$\text{or } A_r(\mathrm{Fe}) : A_r(\mathrm{S}) = 56 : 32 = 7 : 4$$

An amount of iron weighing 7 g contains the same number of iron atoms as the total of sulphur atoms contained in 4 g of sulphur. If we take iron in amount exceeding 7 g, the number of iron atoms will exceed the number of sulphur atoms taken for the reaction. The number of sulphur atoms will be insufficient to react with all the iron atoms, and the excess iron atoms will remain unreacted. If less than 7 g of iron is taken, the excess sulphur atoms will remain unreacted with iron.

Let us consider a case where a mixture of 4 g of sulphur and 10 g of iron is taken for the reaction. All the sulphur will be consumed in the reaction while only 7 grams of iron will react with sulphur. The remaining 3 g of iron will not react, and a mixture consisting of 11 g of iron sulphide (4 g + 7 g = 11 g) and 3 g of unreacted iron will thus be formed instead of pure iron sulphide. If we now grind the mixture into powder, the unreacted iron can be separated by a magnet.

Thus, whatever the initial weights of iron and sulphur may be, the composition of the resultant iron sulphide will always be the same: 4 parts by weight of sulphur will combine with 7 parts by weight of iron. When we obtain water by any known method, and from any initial quantities of oxygen and hydrogen, water will always contain 8 parts of oxygen per 1 part of hydrogen.

The composition of any compound is always one and the same regardless of the method by which it has been prepared. A compound will thus differ from a mixture by a definite known weight proportion of its component chemical element; the proportion of components in a mixture may be varied quite arbitrarily.

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1. 7 g of iron and 7 g of sulphur were taken for a reaction. Which of these substances will be consumed in the reaction completely? What is the weight of the resultant iron sulphide? Which substance has not been reacted? What is the weight of the unreacted residue? Make mental calculations.
2. One atom of zinc combines in zinc sulphide with one sulphur atom. What weights of zinc and sulphur should be taken for their reaction so that zinc sulphide alone will be produced (without admixtures of sulphur or zinc)? (The atomic weight of zinc is 65 and of sulphur 32.)

1.13 Chemical Formula. Molecular Weight

The expression of the composition of a substance by chemical symbols is called the chemical formula of a substance. We obtain formulas of simple substances by writing the symbol of the element and indicating the number of atoms by a *subscript*. Molecules of hydrogen and oxygen contain two atoms each, and their composition is thus expressed by the formulas H_2 and O_2.

In order to write a formula of a compound one must know of what chemical elements the compound is composed, and the number of atoms of one element that combine in this compound with a definite number of the other element's atoms. The formula of a chemical compound is thus expressed by the symbols of chemical elements contained in the compound, and by the subscripts (to the lower right of each symbol). A molecule of water, for example, consisting of two hydrogen atoms and one oxygen atom, is represented by the formula H_2O.

In the case of a solid with a non-molecular structure, its component elements are assumed to be present in the same proportion as in a crystal, e.g. FeS.

What information does a chemical formula contain? A chemical formula indicates if this is a simple substance or a compound, what chemical elements form the substance, and the number of atoms of one element that have combined with a definite number of atoms of another element. But this information is far from exhaustive. What else can be learnt from a formula of a compound? We can calculate the relative molecular weight of a chemical compound (M_r) using its formula.

The relative molecular weight of a substance is the ratio of the molecular weight of a substance to 1/12 the weight of carbon atom.

In order to calculate the relative molecular weight of a substance it is necessary to sum up relative atomic weights multiplied by the number of atoms of each element.

For example, the relative molecular weight of water $M_r\ (H_2O) = 1 \times 2 + 16 = 18$. The weight of a water molecule in atomic mass units (amu) is

$$m_m\ (H_2O) = 2 \times 1 \text{ amu} + 16 \text{ amu} = 18 \text{ amu}$$

If a substance has a non-molecular structure, the relative molecular weight of this substance will be defined as the sum of relative atomic weights of the elements, multiplied by the number of atoms in the formula of this substance. In this case the formula expresses the composition of a conventional molecule of the substance.

The *weight fraction of an element* can be calculated from the chemical formula of the substance. This is the ratio of the weight of atoms of the given element to the weight of the molecule, expressed usually in fractions of unity or in percentages.

The weight of a water molecule is 18 amu, while the weights of hydrogen and oxygen it contains are 2 amu and 16 amu respectively. The weight fraction of hydrogen in water is

$$2 \text{ amu} : 18 \text{ amu} = 0.11 \text{ or } 11 \text{ per cent}$$

The weight fraction of oxygen in water is

$$16 \text{ amu} : 18 \text{ amu} = 0.89 \text{ or } 89 \text{ per cent}$$

The composition of water of any weight will be the same: 89 per cent of oxygen and 11 per cent of hydrogen. The chemical formula of a substance thus expresses the following: (1) the qualitative composition of a substance, i.e. it indicates what chemical elements compose a given substance; (2) the atomic composition of its molecule, i.e. the number of atoms of each element contained in the molecule of this substance.

The chemical formula of a substance can further be used to calculate: (1) the relative molecular weight of a substance and the weight of its molecule in amu; (2) the weight fractions of the elements in a given substance (in per cent).

It is necessary to emphasize certain points when writing chemical formulas. It is essential, for example, to differentiate between $2O$ and O_2. In the former case two separate oxygen atoms are meant, while O_2 indicates that two oxygen atoms are combined in a molecule of gaseous oxygen. If we come across a single O, it indicates one atom of oxygen.

If we want to indicate that two or three molecules of gaseous oxygen are involved in a chemical reaction we write $2O_2$ and $3O_2$ respectively. Four molecules of water are designated as $4H_2O$.

A figure standing before the formula is called the *coefficient* and indicates the number of molecules of a given substance.

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1. Use chemical symbols and formulas to designate one oxygen atom, two oxygen atoms, one molecule of oxygen, two oxygen molecules.
2. What do the following notations mean: 5H, 3C, $7H_2$, $2CO_2$? Calculate the weight of a given number of atoms or molecules in atomic mass units (amu).
3. Which of the following figures referring to the chemical elements, carbon and oxygen, are correct: 8 amu, 24 amu, 32 amu, 47 amu? Why cannot the remaining numbers be referred to these elements?
4. Write the chemical formulas of (a) water, and (b) iron sulphide. Calculate the relative molecular weight of each substance.
5. Can water exist as: (a) 10, (b) 150, (c) 36 atomic mass units? Reason your answer.
6. The relative molecular weights of one compound consisting of carbon and oxygen and another compound of free nitrogen are the same. (A molecule of nitrogen consists of two atoms.) Write down the formulas of these two substances.
7. A compound of nitrogen with oxygen and a compound of carbon with oxygen have the same relative molecular weight of 44. Derive the chemical formulas of these two compounds.
8. Calculate the weight fraction of each element in the substances given below from their chemical formulas: (a) ferric oxide Fe_2O_3, (b) carbon dioxide CO_2, and (c) magnesium oxide MgO.
9. Read the formulas below, perform all the necessary calculations, and decide what information can be derived from them about the given substance: (a) glucose $C_6H_{12}O_6$, (b) sulphuric acid H_2SO_4.
10. A molecule of sugar consists of 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. Write the chemical formula of sugar and calculate its relative molecular weight.
11. Without referring to the table of atomic weights decide which of the following substances contains greater amount of iron: (a) 1 ton of iron sulphide or 1 ton of pyrite (FeS_2); (b) 1 ton of magnetite (Fe_3O_4) or 1 ton of haematite (Fe_2O_3)?
12. We know that sulphur reacts with iron to form iron sulphide. But under certain conditions 7 parts by weight of iron can combine with 8 (not 4) parts by weight of sulphur. Derive the formula of this compound.
13. When sulphur burns it combines with oxygen. The weight of the obtained compound is twice the initial weight of sulphur. Derive the formula of this compound remembering that its molecule has one sulphur atom.

1.14

Valency

Up to now you have used the formulas of substances taken from the textbook. How are formulas of chemical compounds derived? This is done on the basis of information about the quantitative and qualitative composition of substances. It has, for example, been established experimentally that water is formed from 8 parts by weight of oxygen and one part by weight of hydrogen. The minimum quantity of oxygen that a molecule of water may contain is one atom, whose atomic weight is 16 amu. It follows that the molecule of water contains two atoms of hydrogen because the atomic weight of one hydrogen atom is 1 amu. This method is used in cases where the formula of a given substance is determined for the first time.

The number of chemical substances is immense and it would be very difficult to remember all their formulas. But once we know the rules by which atoms of various elements combine into compounds, we can derive the formulas of various compounds. To do this, consider the special property of atoms known as *valency*.

Consider the formulas of some compounds:

$$HCl, \quad H_2O, \quad NH_3, \quad CH_4$$

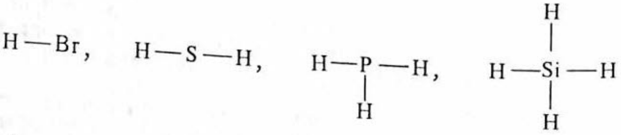
It will be seen from these formulas that one chlorine atom combines with one hydrogen atom, one atom of oxygen with two hydrogens, one atom of nitrogen with three hydrogens, and one atom of carbon with four hydrogen atoms.

The property of atoms to add a definite number of atoms of other elements is called the valency.

The valency of a hydrogen atom was adopted as the unit of valency. A hydrogen atom cannot combine with more than one atom of any other element. This will be seen from chemical formulas of the following compounds

$$HBr, \quad H_2O, \quad PH_3, \quad SiH_4$$

These formulas can be written as follows:



$$H{-}Br, \quad H{-}S{-}H, \quad \begin{array}{c} H{-}P{-}H \\ | \\ H \end{array}, \quad \begin{array}{c} H \\ | \\ H{-}Si{-}H \\ | \\ H \end{array}$$

The dashes designate here bonds between atoms. The presentation is graphical. One can easily see which atoms are connected with one another and which are not. The formula of water shows that both hydrogen atoms are connected with the oxygen atom but are not connected with each other. The above formulas show that atoms of some elements (chlorine, bromine) can combine with one hydrogen atom. These elements are *univalent*. Atoms of other elements (oxygen, for example) can combine with two hydrogen atoms. Hence oxygen atoms are *divalent*, etc.

It can thus be formulated that the valency of atoms of elements in compounds with hydrogen is determined by the number of hydrogen atoms combined with one atom of a given element. Let us compare the valency of hydrogen atoms and oxygen atoms in the molecule of water. The sum of valency units of hydrogen atoms in the molecule of water (2) is equal to the valency of the oxygen atom (also 2). In methane, CH_4, the valency of a carbon atom (4) is equal to the sum of valency units of four hydrogen atoms (also 4). In the molecules of the above compounds, consisting of two elements, the sum of valency units of atoms of one element equals the sum of valency units of atoms of the other element. The valency of a hydrogen atom in all its compounds is 1; in other words, hydrogen is always univalent. The valency of an oxygen atom is always 2, i.e. oxygen is always divalent. We often omit the word 'atom' when we speak of valency and would normally say 'the valency of the element' instead of the 'valency of atoms of the element'.

If the valency of one element in a compound consisting of two elements (binary compound) is known, the valency of the other can easily be calculated. Once we know that the valency of oxygen is always 2, we can easily determine valencies of other elements from their oxides. For example, the formula of phosphorus oxide is P_2O_5. In order to calculate the valency of phosphorus, the total number of valency units of oxygen should first be determined. This can be easily done by multiplying the valency of the oxygen atom by the number of oxygen atoms contained in the molecule of phosphorus oxide: 2 × 5 = 10. The total number of valency units of two phosphorus atoms in this compound must be also 10. Hence the valency of the phosphorus atom is 10 : 2 = 5. It is customary to designate the valency of elements in chemical formulas by writing Roman numerals above their chemical symbols:

$$\overset{V}{P}_2\overset{II}{O}_5$$

Some chemical elements have *constant* valency in all their compounds while other elements have *varying* valencies (see Table 1.2). Sodium and potassium, for example, are always univalent; while oxygen, zinc, magnesium, and calcium are always divalent. Their valency is constant. Among the metals, which we shall very frequently deal with in this course of inorganic chemistry, copper and iron have varying valencies. Depending on the other element with which these atoms with varying valency combine, and also on the conditions under which the reaction occurs, they display this or that valency.

Table 1.2

The Valency of Some Elements

Valency	Metals	Nonmetals
(univalent) I	**Na**, **K**, Ag, Cu, Hg	**H**, Cl
(divalent) II	**Mg**, **Ca**, **Ba**, Cu, Hg, Fe, **Zn**, Sn, Pb, Cr	**O**, S
(trivalent) III	**Al**, Cr, Fe	N
(tetravalent) IV		C, S, Si
(pentavalent) V		N, P
(hexavalent) VI		S

Note. Elements with constant valency are given in bold type.

In order to specify the varying valency of an element in a particular compound, a Roman numeral is given in parenthesis after the symbol of the element: $FeCl_2$ is iron(II) chloride, $FeCl_3$ is iron(III) chloride, SO_3 sulphur(VI) oxide, SO_2 sulphur(IV) oxide, etc.

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1. Write the formulas of hydrogen compounds mentioned in this section and use Roman numerals to designate the valencies of the elements combined with hydrogen.
2. Write down formulas and use Roman numerals to designate the valency of elements in the following compounds: (a) Al_2S_3, Na_2S, MgS, CS_2, Cu_2S, PbS, Ag_2S, ZnS (sulphur is divalent in these compounds); (b) KCl, $CaCl_2$, $FeCl_3$, CCl_4, PCl_5, $ZnCl_2$, $CrCl_3$, and $SiCl_4$ (chlorine is univalent).
3. What is the valency of: (a) copper in its oxides Cu_2O and CuO; (b) iron in FeO and Fe_2O_3?
4. What elements with a constant valency of 1 and 2 do you know?

1.15 Derivation of Formulas by Valency

Once the valency of the elements is known, formulas of binary compounds can be derived. Let us derive, for example, the formula of aluminium oxide, knowing that aluminium is trivalent. Superscribe the Roman numerals III for aluminium and II for oxygen: $\overset{III}{Al}\overset{II}{O}$. The least common multiple of the numbers representing the valency of aluminium and oxygen (3 and 2) is 6. In order to determine the number of aluminium and oxygen atoms, divide the least common multiple by the valency of aluminium (3) to obtain 2 ($6:3=2$). The required number of aluminium atoms is 2. Now divide the same multiple 6 by the valency of oxygen (2) to obtain 3 ($6:2=3$). The required number of oxygen atoms is 3. Now write the symbols of aluminium and oxygen again and subscribe the number of atoms of each element. The required formula is Al_2O_3. Let us check if the sum of valency units of aluminium is the same as that of oxygen. Multiply the valency of each element by the number of its atoms to obtain: $3 \times 2 = 2 \times 3$. The products are equal which means that the formula is correct. Thus, in order to derive a chemical formula of a substance from the valency of its component elements it is necessary: (1) to write the chemical symbols representing these elements and superscribe the valency of each element by the Roman numerals, (2) to find the least common multiple of the numbers expressing their valency, (3) to divide the least common multiple by the valency of each element, and (4) to subscribe the obtained index to the right side of the element.

? △

1. Using Table 1.2, derive formulas for the following compounds:

(a) Ca_xCl_y, $Mg_x\overset{III}{N}_y$, $Al_x\overset{II}{S}_y$, $\overset{III}{Fe}_xCl_y$, C_xCl_y;
(b) Mg_xSi_y, Si_xO_y, Ca_xP_y, Si_xCl_y, Al_xCl_y.

2. Determine the formulas of compounds formed by oxygen and the

following elements: (a) Mn(VII), Cr(VI), Sb(V), Sn(IV), Cr(III), N(II), Hg(I); (b) Cl(VII), S(VI), As(V), Pb(IV), B(III), Sr(II), Cu(I). The chemical symbol of oxygen in these formulas is written second.

1.16 The Theory of Atoms and Molecules in Chemistry

We have learnt that the molecular theory explains physical phenomena occurring with substances. The atomic theory helps the molecular theory to explain chemical phenomena. The two theories are combined in one theory of atoms and molecules. The essence of this theory can be expressed in the form of a few propositions:

1. A substance is not divisible to infinity, but only to the level of its molecules.
2. Molecules remain unaltered in physical phenomena and are destroyed in chemical phenomena.
3. Molecules of substances consist of atoms; atoms, unlike molecules, remain unaltered in chemical reactions.
4. Atoms of each type (element) are alike but differ from atoms of any other type (element), for example in their weight.
5. A chemical reaction consists of the formation of new substances from the atoms of which the initial substances were composed.

The atomic theory can be traced back to ancient Greece (i.e. to the pre-Christian era). The ancient philosophers abandoned the belief in God or miracles and tried to explain all mysterious natural phenomena by ordinary causes – the combination and separation, migration and mixing of invisible particles, atoms, that have existed eternally. The atomic theory was persecuted for centuries by the church as contradicting the belief in God. The supporters of the new theory were condemned and their books were burned. But the ancient philosophers gave the name of atoms to the particles that we now call molecules. They could therefore only explain physical phenomena such as wind, storm, propagation of odour, evaporation of water, etc.

The fundamentals of the theory of atoms and molecules were formulated in the middle of the 18th century by the great Russian scientist M. V. Lomonosov, who declared the study of the structure of substances as the main subject of chemistry. But the theory of atoms and molecules was universally accepted only early in the 19th century when J. Dalton worked out his theory of the atomic weights of elements.

Chemistry became a genuine science only after scientists began interpreting chemical reactions from the viewpoint of the theory of atoms and molecules.

?
△

1. In 1745 M. Lomonosov wrote: "The *element* is a part of the *body*, which does not consist of any smaller particles that can differ from one another... *Corpuscles* are accumulations of the *elements* into a small mass... *Corpuscles* are identical if they consist of the same number of the same elements which are similarly interconnected... *Corpuscles* are different when their component elements differ and

Mikhail Vasilievich LOMONOSOV (1711–1765)

The great Russian scientist. He was born into the family of a fisherman. The Russian poet Alexander Pushkin wrote that Lomonosov was "a historian, rhetorician, mechanic, chemist, mineralogist, artist, and a poet; he tried everything and was a success in all he did". Lomonosov substantiated the law of conservation of mass and explained the essence of metal roasting. He formulated the main principles of atomic-molecular science, introduced quantitative methods of investigation into chemistry, and united chemistry with physics to give a new science, physical chemistry. He used to say: "Without knowledge of the internal structure of imperceptible particles physicists, and especially chemists, wander in the dark".

John DALTON (1766–1844)

An outstanding English scientist. He was the son of a weaver and studied physics and mathematics by himself. At the age of 12 he became a teacher at a village school. He introduced the concept of atomic weights and thus contributed much to the development of the theory of atoms. He was also the first to use chemical formulas and succeeded in calculating the composition of substances from these formulas (his formulas differed, however, from those we use now).

are interconnected in a different way or in different numbers; this accounts for the infinite variety of *bodies*." (Emphasis added by the authors). Compare these formulations with modern concepts of molecules and atoms. Replace the underlined words (element, body, corpuscle) by the corresponding words that we would use now (substance, molecule, atom).

2. Rewrite the sentences given below and fill in the blanks with the following words: molecule (molecules), atom (atoms).

(a) Air is a mixture containing .... of oxygen.

(b) .... of water contain .... of oxygen.

(c) When oxygen is dissolved in water, ... of oxygen are distributed among .... of water.

(d) The weight of an oxygen ...... is twice as great as the weight of an oxygen ....

(e) Animals breathe .... of oxygen.

(f) ...... of sugar contained in jam account for its sweet taste.

(g) A .... of water consists of .... of oxygen and hydrogen.

(h) We smell the odour of an iodine tincture because ...... of iodine are volatile and evaporate from it.

3. Before the theory of atoms and molecules was formulated, alchemists of the Middle Ages tried in vain to convert base metals into gold. Using the atomic theory prove the futility of their attempts.

1.17 The Law of Conservation of Mass (Weight)

The products of any chemical reaction consist of the same atoms that composed the starting materials (reactants). The atoms are not changed during the chemical reactions and it means that the weight of all atoms involved in the reaction should remain unchanged. If this is so, then the products of any chemical reaction should have the same weight as the total weight of all the starting materials before the reaction. At first sight, the results of some experiments might contradict this law. Take, for example, metal. If we roast it in air, it turns into brittle scales whose weight exceeds the starting weight of the metal. It can be guessed that the metal has joined with some particles from the surrounding air. How can we prove it? M. Lomonosov found a correct solution to this problem. Instead of heating metal in air he placed it in a sealed vessel and heated it (Fig. 1.12). The metal turned into scales, whose weight usually exceeded the weight of the starting metal. But when Lomonosov weighed the sealed vessel containing the burnt metal he found that the weight of the vessel remained the same. This proved that the weight of the air contained in the sealed vessel decreased by the same amount, that the weight of the burnt metal had increased.

The mass (weight) of substances entering into a chemical reaction is always equal to the mass (weight) of the reaction products. This is the main law of chemistry called the law of mass (weight) conservation. Lomonosov formulated it as follows:

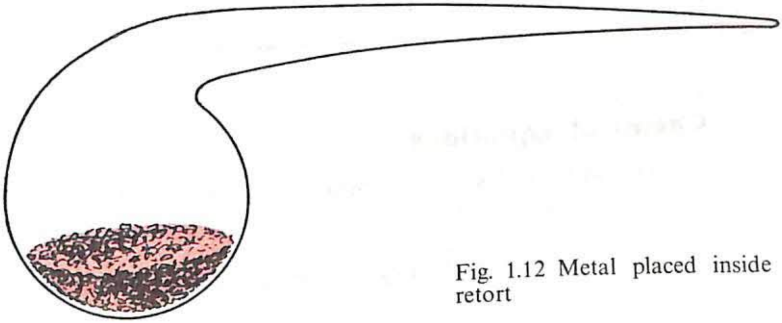

Fig. 1.12 Metal placed inside a sealed retort

"All changes occurring in nature can be described as follows: if a body loses some of its weight, the same weight will be added to some other body; and if some portion of matter is lost it means that matter will be gained at some other place."

It follows from the law of conservation of mass that matter can be neither created from nothing nor transformed into nothing. Therefore, if it seems to us that the product of a chemical reaction has been formed from nothing or disappears leaving no trace, it means that some substances involved and obtained in the reaction were not taken into consideration or overlooked. When, for example, a log of wood burns, an inexperienced observer may conclude that it is destroyed almost completely. A detailed study of this reaction shows that the weight of substances consumed in the reaction of wood burning (wood itself and oxygen of the air) is equal to the weight of water, carbon dioxide, and ash that are then formed. Nothing can be made from nothing and no substance can be destroyed to nothing.

Using the law of conservation of mass it is possible to calculate the weight of any reactant, or any product of the reaction, provided the weights of all other substances involved in the reaction are known. For example, if we want to find out the weight of oxygen obtained by decomposition of a certain portion of mercury oxide, it is not necessary to collect the oxygen and weigh it. It will be sufficient to weigh the starting quantity of mercury oxide and the mercury obtained in the reaction. According to the law of mass (weight) conservation the sum of weights of mercury and oxygen equals the weight of the starting mercury oxide. The weight of oxygen obtained is thus the weight of mercury oxide less mercury obtained in the reaction. Take, for example, 2.17 g of mercury oxide and decompose it to mercury and oxygen. Weigh the obtained mercury: its mass is 2.01 g. The weight of oxygen obtained in the reaction will then be

$$2.17\ \text{g} - 2.01\ \text{g} = 0.16\ \text{g}$$

?
△

1. Formulate the law of conservation of mass.
2. Mercury(II) oxide was decomposed to give 16 g of oxygen and 201 g of mercury. What was the starting weight of mercury(II) oxide?
3. When M. Lomonosov broke the tip of the vessel in which he had roasted the metal, the weight of the vessel (together with the broken tip) proved to be greater than the weight of the vessel and metal before roasting took place. Explain.

1.18 Chemical Equations

If chemical formulas of all substances involved and obtained in the reaction are known, the chemical reaction can be expressed by a *chemical equation*.

A chemical equation is the representation of a chemical reaction by means of chemical formulas.

To draw a chemical equation of water decomposition reaction, for example, write the formula of the starting substance (or formulas if there are several of them) to the left, and the formulas of the substances produced in the reaction (reaction products) to the right. The formulas of the starting and resultant substances are joined by the symbol "+":

$$\begin{array}{lll} \text{water} & \rightarrow & \text{hydrogen} + \text{oxygen} \\ H_2O & \rightarrow & H_2 + O_2 \end{array}$$

We must put the coefficients before the formulas so that the number of atoms involved in the reaction should (according to the law of mass (weight) conservation) be the same as that of the resultant products. In other words the equation should be 'balanced'. Reason as follows: to form one diatomic molecule of oxygen (O_2) two atoms of oxygen are required; in order to obtain them we have to decompose two molecules of water. Hence put the coefficient 2 before the formula representing water:

$$2H_2O \rightarrow H_2 + O_2$$

The number of oxygen atoms is now equal on both sides of the equation. But the number of hydrogen atoms remains unbalanced. Decomposition of two water molecules gives four hydrogen atoms (two diatomic hydrogen molecules). It means that the coefficient 2 should be put before the H_2 molecule on the right-hand side. The number of hydrogen and oxygen atoms is now the same on both sides of the chemical equation and we can replace the arrow by the equality sign:

$$2H_2O = 2H_2 + O_2$$

The equation shows that each pair of water molecules consisting of two hydrogen and one oxygen atoms gives two diatomic molecules of hydrogen in this reaction and one diatomic molecule of oxygen.

Unlike algebra, the sides of a chemical equation cannot change places because the sense of an inverted equation will be quite different. For example, we change places in the equation $2H_2O = 2H_2 + O_2$ to obtain $2H_2 + O_2 = 2H_2O$. The new equation expresses quite a different reaction that can only be realized under different conditions. The former equation expresses the reaction of water decomposition; the latter the reaction of combination of oxygen with hydrogen.

The given example can be used to formulate the following rule: in order to draw a chemical equation, the formulas of the reactants should be written on the left and the formulas of reaction products on the right, and the plus sign should be placed in between them.

The number of atoms of each element on the left-hand side should be the same as on the right-hand side of the equation. In order to balance the equation proper coefficients should be placed.

? 1. Read the equation of the reaction between oxygen and hydrogen. What does this equation mean?

△ 2. Write an equation for the reaction of decomposition of mercury oxide (HgO) knowing that two substances, namely mercury (Hg) and oxygen (O_2), are obtained.

3. Fill in the missing coefficients in the following equations of chemical reactions:

(1) $2Zn + O_2 = ?ZnO$
(2) $?Fe + 3Cl_2 = ?FeCl_3$
(3) $?Ag + S = Ag_2S$
(4) $?Na + Cl_2 = 2NaCl$
(5) $?Mg + O_2 = 2MgO$
(6) $2Al + ?Cl_2 = 2AlCl_3$
(7) $?Al + ?S = Al_2S_3$
(8) $?Al + ?O_2 = 2Al_2O_3$

Check if the number of each element on the left and right parts of the equations is the same.

1.19 Types of Chemical Reactions

Chemical reactions can be divided into several main types.

Decomposition reactions. Put powdered malachite (a green substance) into a test tube (Fig. 1.13), close it with a stopper through which a glass tube (bent at a right angle) is passed, and lower the end of the tube into a beaker containing a small amount of lime water. Heat the malachite in the test tube over a burner: the green malachite turns black. This is copper oxide (CuO) with which we are already acquainted. Droplets of water precipitate on the test tube walls and the solution in the beaker becomes cloudy. We have already learnt that carbon dioxide turns lime water cloudy. What has happened to the malachite? It has decomposed to give three new substances, viz. copper oxide, water, and carbon dioxide:

malachite = copper oxide + water + carbon dioxide

$$Cu_2CH_2O_5 = 2CuO + H_2O + CO_2$$

Malachite has decomposed. One substance has formed three new substances.

Let us remember the reaction of decomposition of water:

water = hydrogen + oxygen

$$2H_2O = 2H_2 + O_2$$

These two reactions are characterized by a common feature: one starting substance gives several reaction products (water gives two, and malachite three new substances).

A chemical reaction during which one substance gives several new substances is called the reaction of decomposition.

?

△

1. Can simple substances undergo a reaction of decomposition? Reason your answer.
2. Can a reaction of decomposition give (a) simple substances, (b) compounds? Give examples.

Addition reactions. If decomposition alone were to occur in nature, all composite substances (compounds) would have long ago decomposed and chemical phenomena would not occur any longer. But there exist other reactions in nature.

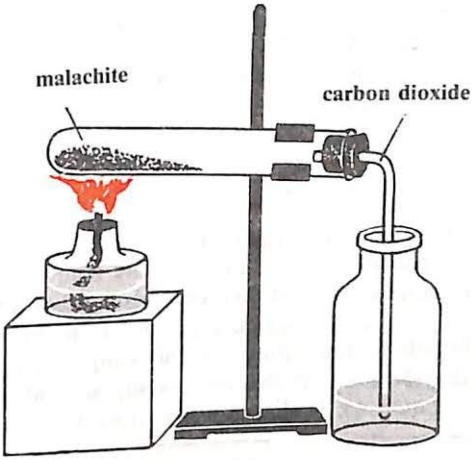

Fig. 1.13 Decomposing malachite

When copper is heated in air it becomes coated with a black film: copper is transformed into copper(II) oxide:

copper + oxygen = copper(II) oxide

$2Cu + O_2 = 2CuO$

Remember the reaction in which iron(II) sulphide (ferrous sulphide) is obtained:

iron + sulphur = ferrous sulphide

$Fe + S = FeS$

The reactions seem different but they have one thing in common: several substances (in our examples, two substances) give one new substance. **Reactions in which several substances give one new substance are called addition reactions.**

Thus the addition reactions are the opposite of the reactions of decomposition.

?

1. Can an addition reaction give a simple substance? Explain your answer.

Substitution reactions. Consider another type of chemical reactions. (We have not yet come across such a reaction.)

Place a blue solution of copper(II) chloride ($CuCl_2$) in a test tube and immerse an iron nail in the solution. The nail will very soon become covered with copper, while the solution will by the end of the reaction become greenish, because it will now contain iron(II) chloride $FeCl_2$ instead of copper(II) chloride. The reaction can be expressed as follows:

iron + copper(II) chloride = copper + iron(II) chloride

$Fe + CuCl_2 = Cu + FeCl_2$

If pieces of zinc (Zn) are dropped into the solution of copper(II) chloride, copper will be liberated as in the reaction with iron. The solution will now turn colourless because the other product of the reaction is zinc chloride $ZnCl_2$ which is colourless. The equation of the reaction is as follows:

$$\begin{array}{llll} \text{zinc} & + \text{copper(II) chloride} & = \text{copper} & + \text{zinc chloride} \\ Zn & + CuCl_2 & = Cu & + ZnCl_2 \end{array}$$

The atoms of copper in copper(II) chloride have been replaced by the atoms of iron in the first case and by zinc atoms in the second case. We can thus conclude that atoms can also substitute for one another in compounds. **Chemical reactions between a simple substance and a compound, in which the atoms of the simple substance replace the atoms of one of the elements in the compound, are called substitution reactions.**

Later we shall get acquainted with one more type of chemical reactions.

? 1. Place a mixture of powdered mercury(II) oxide and copper in a test tube and heat. Write the equation of the chemical reaction knowing that two substances (both are already known to you) are formed; one of them is a simple substance and the other is a compound. Describe the signs of the reaction (they are two). What is the type of the reaction?

△ 2. What types of reactions do you know? Give examples of each type of chemical reactions.

3. Write down the reactions given below, replace the question mark by the appropriate coefficient, and indicate the types of the reactions:

(1) $?P + ?O_2 \rightarrow 2P_2O_5$

(2) $?HgO \rightarrow ?Hg + O_2$

(3) $?Mg + O_2 \rightarrow ?MgO$

(4) $Zn + ?HCl \rightarrow ZnCl_2 + H_2$

(5) $CaCO_3 \rightarrow CaO + CO_2$

(6) $Mg + CuCl_2 \rightarrow MgCl_2 + Cu$

4. Which substances can be neither decomposed nor obtained by addition reactions?

5. Write the equations for addition reactions between sulphur and the following metals: (a) magnesium Mg, (b) zinc Zn, (c) silver Ag, (d) aluminium Al, knowing that the formulas of the obtained compounds are MgS, ZnS, Ag_2S and Al_2S_3.

6. Write down equations for decomposition reactions of the following compounds:
(a) platinum oxide PtO_2, (b) silver oxide Ag_2O, (c) mercury(I) oxide Hg_2O, and (d) gold oxide Au_2O_3.

7. Place a copper coin in a solution of corrosive sublimate ($HgCl_2$). A substitution reaction takes place. Write the equation of the reaction and describe the signs of the reaction (two) knowing that corrosive sublimate is a colourless substance and the formula of the resultant compound is $CuCl_2$.

8. The red pigment minium Pb_3Q_4 can be obtained (a) by heating lead oxide PbO_2 (which gas is evolved during this reaction?), and (b) by heating the yellow pigment PbO (what gas is absorbed from air for the reaction?). Write equations for both reactions. What types of reactions are they?

2

Oxygen. Oxides. Burning

2.1

Oxygen

We have become acquainted with the basic concepts of chemistry and now can proceed to the study of important chemical elements and their compounds. We shall begin with oxygen, because oxygen is the most abundant element in the Earth's crust, in water and the atmosphere. All living organisms consume molecular oxygen for breathing; burning, this very important and frequently occurring natural reaction, also consumes oxygen.

At the end of the eighteenth century, an English scientist John Priestley studied various substances during heating. He used a magnifying glass to collect the sun's rays to heat mercury(II) oxide in the apparatus shown in Fig. 2.1. Much gas evolved and John Priestley thought it was air. But when he put a burning candle into the vessel containing the gas collected he witnessed an unusual phenomenon which made a great impression on him: the candle began emitting a very bright light.

Priestley placed one mouse into a vessel containing ordinary air and another into a vessel filled with the obtained gas. The mouse in the first vessel soon died from suffocation while the other mouse was as lively as before. Priestley tried breathing the gas and found it both easy and pleasant to breathe. The gas was oxygen.

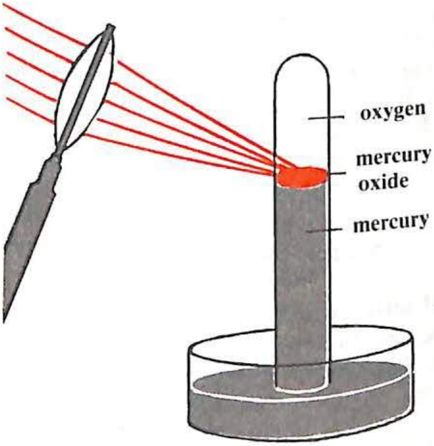

Fig. 2.1 Priestley's experiment

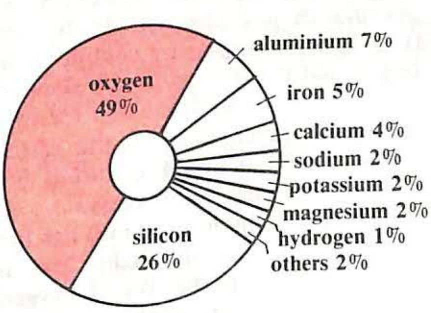

Fig. 2.2 Occurrence of elements in the Earth's crust (in per cent by weight)

The chemical symbol of oxygen is O. Its atomic mass (weight) is 16. The valency of oxygen in compounds is constant and equals 2. The oxygen molecule O_2 consists of two atoms. The molecular weight of oxygen is therefore 32.

Oxygen is the most abundant element in nature (Fig. 2.2). It is contained in the free state in air. But the greatest amounts of it are contained in the compounds that make up rocks, minerals, and water. Oxygen constitutes about 50 per cent of the weight of the Earth's crust (water and air included). Oxygen is also contained in the chemical compounds that build the animals and plants.

? 1. In what form is oxygen contained in the atmosphere, natural waters, and in the Earth's crust? Is it in the form of a simple substance or in compounds with other elements?

△ 2. Calculate the weight fraction of oxygen in water H_2O and in river sand SiO_2.

3. What properties of oxygen do you know from your experience?

2.2 Properties of Oxygen

Oxygen is a colourless gas without odour or taste. It is slightly heavier than air and is sparingly soluble in water. Under a pressure of 101.3 kPa and a temperature of $-183\,^{\circ}\mathrm{C}$ oxygen is converted into a liquid state. Liquefied oxygen is a blue mobile liquid.

Let us study the properties of oxygen in chemical reactions. We can easily identify oxygen because it supports the burning of combustible materials. When a glowing splint is put into oxygen it takes flame. Let us consider some reactions of oxygen with simple substances.

1. Place a pinch of red phosphorus in an iron spoon. Red phosphorus is a simple substance; it is insoluble in water; its colour is red. Put the spoon containing phosphorus in oxygen. No reaction takes place. Set fire to the phosphorus and again lower the spoon into the vessel filled with oxygen (Fig. 2.3 *c*). Phosphorus continues burning in oxygen but the flame is so bright that the eye can hardly stand it. The vessel becomes filled with a white smoke, which is so dense that the spoon soon becomes invisible. After a time the smoke precipitates on the vessel walls as a white powder. Add some water. First the liquid is turbid but the powder soon dissolves and the solution becomes clear again.

The red insoluble substance has turned into a white soluble substance with liberation of heat and light. This indicates that a chemical reaction has occurred. What is the role of oxygen in this reaction? We can suggest that phosphorus might combine with oxygen in this reaction. If this is an addition reaction, oxygen must be consumed in it together with phosphorus. Let us try to prove that our suggestion is correct.

To do so, burn another portion of red phosphorus in oxygen but not in an open vessel as in our previous experiment, but in a bell jar (see Fig. 2.13)

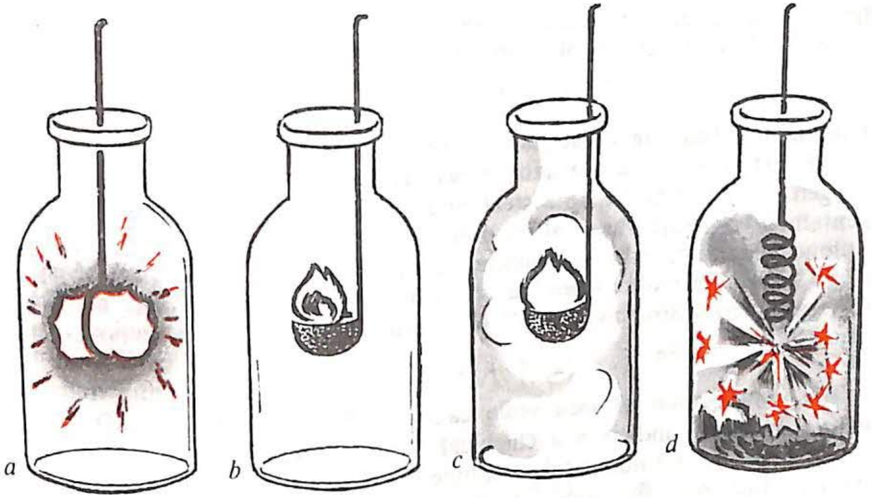

Fig. 2.3 Burning in oxygen of (*a*) carbon; (*b*) sulphur; (*c*) phosphorus; and (*d*) iron

lowered in water. Pass the wire handle of the spoon through the stopper of the bell jar. Ignite the phosphorus, place the spoon into the bell jar and close it with the stopper. As the phosphorus burns, the water level rises in the bell jar. This indicates that the amount of oxygen decreases. It is consumed in the reaction.

We have thus proved that oxygen combines with phosphorus to form a new product. This is phosphorus(V) oxide P_2O_5.

2. Using an iron spoon, put a small piece of coal into the flame of burner. When the coal becomes hot, remove it from the flame and keep it in the air: it glows for a short while and then dies out. Coal does not readily burn in air. Hold the coal in the flame again and then put it in a bottle filled with oxygen (Fig. 2.3 *a*). The glowing coal will not be extinguished as in air but will turn white-hot and burn without flame or smoke and diminishes in size until it stops burning. Now introduce a burning splint into the bottle. The flame of the splint will be quenched. Pour lime water into the bottle: it will become cloudy indicating the presence of carbon dioxide CO_2 or carbon(IV) oxide.

A chemical reaction has thus taken place: oxygen has combined with carbon according to this equation

$$C + O_2 = CO_2\uparrow$$

An upward pointing arrow indicates that the product liberated in the reaction is gaseous.

3. Ignite sulphur in a spoon. When in air, it burns with a low blue flame. Now lower the spoon into the bottle filled with oxygen: the burning is more energetic (Fig. 2.3 *b*). Sulphur burns in oxygen with a beautiful blue flame to give sulphur dioxide or sulphur(IV) oxide. The gas differs from carbon

dioxide: its odour is pungent and suffocating. The formula of sulphur dioxide is SO_2. The reaction of sulphur burning in oxygen is expressed as

$$S + O_2 = SO_2\uparrow$$

The rate of burning of substances in pure oxygen is higher than in air.

4. Substances that are usually considered incombustible, e. g. iron, burn in oxygen. Attach a match to a steel wire, light it, and lower it into the bottle containing oxygen: like coal, iron burns without flame or smoke but with a loud cracking, expelling molten iron droplets in the form of sparks (Fig. 2.3 *d*). The molten droplets are scales of iron oxide Fe_3O_4. Iron burns in oxygen according to the following reaction

$$3Fe + 2O_2 = Fe_3O_4$$

The composition of iron scale can also be expressed as $FeO \cdot Fe_2O_3$ where the point indicates a chemical bond between particles.

Most metals and nonmetals combine with oxygen like coal, sulphur, phosphorus, and iron. But these reactions are not obligatory accompanied by burning. Copper, for example, combines with oxygen during heating to turn into a black powder of copper(II) oxide CuO without burning. This reaction can be represented as follows:

$$2Cu + O_2 = 2CuO$$

Oxygen in the free state is one of the most active substances that readily enters into various chemical reactions.

?
Δ

1. Name (a) physical and (b) chemical properties of oxygen.
2. Describe the burning in oxygen of the following substances: (a) phosphorus, (b) coal, (c) sulphur, (d) iron. What products are obtained in these reactions? Describe their properties. What types of reactions are they?
During World War I, shells filled with phosphorus were used, why?
3. What information about substances can be derived from the formulas of carbon dioxide, sulphur dioxide, iron scale?
4. Write equations for chemical reactions between oxygen and the following elements: magnesium Mg, zinc Zn, silicon Si, tungsten W, arsenic As, knowing that the formulas of these oxygen compounds are MgO, ZnO, SiO_2, WO_3, and As_2O_3.
5. Will a vacuum be created if an iron wire or coal are burnt in a sealed bottle containing oxygen? Explain your answer.

2.3 Oxidation. Oxides

Chemical reactions of oxygen with substances are called oxidation reactions, while the products obtained in these reactions are called oxides.

Oxide is a binary compound consisting of atoms of two elements one of which is an oxygen atom.

Phosphorus burns to oxidize into phosphorus(V) oxide P_2O_5. Coal, sulphur, and iron burn to give oxides as well, namely, carbon dioxide CO_2 (the oxide of carbon(IV)), sulphur dioxide SO_2 (the oxide of sulphur(IV)), and iron scale Fe_3O_4 (composed of iron(II) and iron(III) oxides).

Metal oxides, like iron scale and copper(II) oxide, are solids. Oxides of nonmetals may be solid (phosphorus(V) oxide), liquid (water), or gaseous (sulphur dioxide and carbon dioxide under normal conditions).

Oxides are formed by the oxidation with oxygen of simple substances and of some compounds as well. Light a candle and place it into the bottle containing oxygen. The candle burns with a bright flame and droplets of water precipitate on the bottle walls. Water is the oxide of hydrogen H_2O. Add lime water: it turns cloudy. This sign is known to indicate the presence of carbon dioxide, the oxide of carbon(IV). The candle is made of paraffin which consists of carbon and hydrogen elements. When a candle burns, carbon and hydrogen react with oxygen to give water:

$$\text{paraffin} + O_2 \rightarrow CO_2 + H_2O$$

Let us make out the equation for the reaction of oxidation of compounds using the reaction of acetylene burning as an example:

$$\begin{array}{llll} \text{acetylene} & + \text{oxygen} \rightarrow & \text{carbon dioxide} & + \text{water} \\ C_2H_2 & + O_2 \quad \rightarrow & CO_2 & + H_2O \end{array}$$

First we must determine the number of (a) molecules of carbon dioxide and (b) water molecules that are formed by oxidation of one molecule of acetylene. A molecule of C_2H_2 has two carbon atoms and a molecule of CO_2 has one carbon atom. This means that one molecule of acetylene gives two molecules of carbon dioxide. The C_2H_2 molecule has two hydrogen atoms and the molecule of water also has two hydrogen atoms. Hence one acetylene molecule will give one water molecule:

$$C_2H_2 + O_2 \rightarrow 2CO_2 + H_2O$$

Let us now determine the number of oxygen atoms that will be required to form two molecules of carbon dioxide and one water molecule. This number should be equal to the number of oxygen atoms contained in these molecules: 5 oxygen atoms. Five oxygen atoms will be sufficient to build 2(1/2) molecules of oxygen. We have thus found the coefficients:

$$C_2H_2 + 2(1/2)\,O_2 = 2CO_2 + H_2O$$

But a fractional number of molecules 2(1/2) is nonsense. Let us multiply all coefficients by 2. Then:

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

Let us check the equation: there are 4 carbon atoms, 4 hydrogen atoms, and 10 oxygen atoms on the left-hand side of the equation; the number of atoms of these elements on the right-hand side is the same.

? 1. Write equations for the reactions of burning of (a) hydrogen sulphide H_2S, (b) carbon disulphide CS_2, (c) methane CH_4. Will any odour be smelt during burning of (a) methane, (b) hydrogen sulphide, or (c) carbon disulphide? Reason your answer.

△ 2. Write the equation for the decomposition of copper ore azurite $Cu_3C_2H_2O_8$ (only the oxides that are already known to us will be obtained in the reaction).

3. What oxides do you know which are: (a) gaseous, (b) liquid, (c) solid? (The three states of aggregation are understood under normal conditions of pressure and temperature.)

4. Write out the formulas of oxides formed from the following substances: SO_3, H_2SO_4, Na_2SO_4, ZnO, $ZnSO_4$, NO_2, HNO_3, KNO_3.

5. Write the formula of a compound consisting of carbon and hydrogen whose molecular weight is equal to the atomic weight of oxygen. Write the reaction equation for burning of this compound.

2.4 Flame

Most fuels burn with a flame. A flame is hot, luminous gas or vapour. In order to study the structure of a flame use a paraffin candle. Paraffin, as we already know, is a compound consisting of carbon and hydrogen elements. Light a candle and observe the flame. We can distinguish three zones of the flame: the inner, darker zone round the wick, a luminous cone, and the outer barely distinguishable envelop (Fig. 2.4). The wick itself does not burn (except for its bent end).

Let us examine the composition of each zone of the flame. If a glass tube is introduced into the innermost portion of the flame (Fig. 2.5), a white smoke will escape from it. The smoke is paraffin vapour. It can be ignited. We can thus conclude that the inner dark cone of the flame is formed by paraffin vapour.

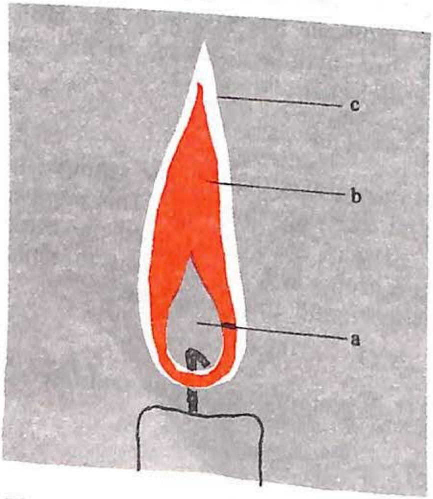

Fig. 2.4 Structure of a candle flame: *a* – inner dark zone; *b* – middle luminous cone; *c* – outer zone

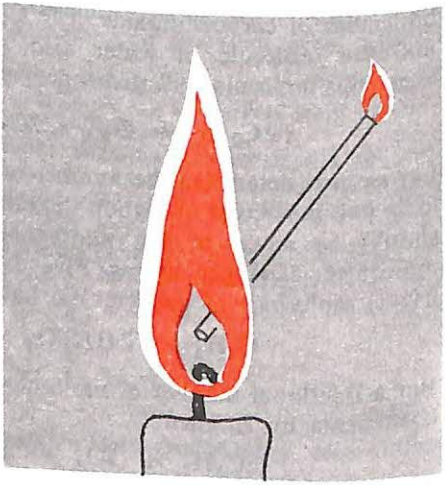

Fig. 2.5 Burning of paraffin vapour withdrawn from the inner zone of the flame

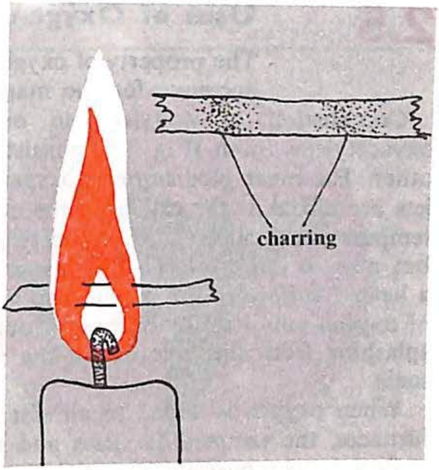

Fig. 2.6 Charring a splint in the flame of a candle

Put a cold object, a porcelain cup, for example, into the middle zone of the flame, the luminous cone. The cup surface will become coated with soot, which indicates that the luminous cone contains free carbon. The composition of the outer cone of the paraffin flame is already known: there are the products of paraffin combustion, namely water vapour (steam) and carbon dioxide.

Put a splint into the flame for a short time as shown in Fig. 2.6. The splint will only char where it contacts the outer cone of the flame. This indicates that this cone has the highest temperature in the flame.

Why is carbon present in the middle zone of the flame? When we put a burning match to the wick, paraffin melts and evaporates. Vapours rise from the wick and ignite. The high temperature of the middle zone decomposes the paraffin vapour into carbon and hydrogen *. Hydrogen burns due to air supplied into the zone from below. Energy, liberated during the combustion of hydrogen, heats carbon particles to a white hot which accounts for luminosity of the flame. As these particles move to the outer zone of the flame they burn, turning into carbon(IV) oxide. Luminosity of the flame here decreases while the temperature rises.

If air is blown into the flame through a glass tube, the flame becomes almost non-luminous and soot does not precipitate on a porcelain cup. This is explained by the abundance of air favouring rapid combustion of carbon particles which therefore are not retained in the flame. The flame in any furnace is formed in the same way.

?

1. Name (a) physical phenomena and (b) chemical reactions which accompany the process of a candle burning.

△

2. Describe the structure of flame and experiments by which the composition of its zones may be established. Which of the flame zones has the highest temperature?
3. Put a burning candle in the sunlight. Hold a sheet of paper behind the candle and observe the shadow of the flame on the paper. This is the shadow of the luminous zone of the flame. Explain.
4. Do all substances burn with a flame?
5. How can a flame giving no soot be made?

---

* To be more exact, the paraffin vapour is decomposed into carbon, hydrogen, and simpler hydrocarbons (compounds of hydrogen and carbon). The latter are volatile.

2.5 Uses of Oxygen

The property of oxygen to support combustion and breathing accounts for the many uses of this gas (Fig. 2.7).

Combustion of acetylene in oxygen is used to weld metals. An oxyacetylene torch (Fig. 2.8) consists of two tubes placed one inside the other. The inner pipe supplies oxygen and the outer acetylene. The two gas jets are mixed at the exit from the nozzle and lit. The flame is white and its temperature is 3000°C. An oxyacetylene torch can be used not only to weld but also to cut steel. To do this, a strong jet of oxygen is directed onto a heated surface of the metal. Iron is known to burn in oxygen, and the jet of oxygen cuts steel by burning it out (as in drilling). The shower of sparks splashing from the hole cut in the metal consists of melted drops of iron scale.

When oxygen is added to air, for example during iron smelting in blast furnaces, the temperature rises and the process is accelerated.

Porous combustible materials such as saw dust, dry moss, or coke impregnated with liquid oxygen burn instantaneously. If the combustion occurs in a closed space, hot gases that are formed, destroy the surrounding objects. Mixtures of porous materials with liquid oxygen (liquid oxygen explosives) are therefore used as explosives in mining and other industries where an explosion may do useful work: construction of tunnels, railroads, hydroelectric power station dams, etc. Liquid oxygen is used as an oxidant in rocket fuels.

If we exhale air onto a dry cold object, droplets of water precipitate on it. If the exhaled air is passed through lime water, it becomes cloudy. As in the burning of a candle continuous oxidation of substances by oxygen occurs in our body and the resultant products are also the same: water and carbon dioxide. Energy is liberated during this oxidation process, and is required to maintain our lives.

Oxygen is necessary for breathing. It is therefore used in cases where the oxygen content in air is deficient. Firemen are provided with special gas masks by which they are protected from smoke or poisonous atmosphere and breathe oxygen from a balloon. People working at high altitudes with oxygen deficit and rarefied air also use special masks and oxygen balloons.

Oxygen is used in medicine to facilitate the breathing of patients with grave diseases or impaired breathing function. Oxygen is dispensed in rubber bags at pharmacy shops for treatment of patients at home. At hospitals special tents are available in which a patient is placed and oxygen delivered from a cylinder.

Oxygen is consumed in large amounts in industry and demand for it increases each year.

Oxygen is obtained industrially from air. For this purpose air is cooled to low temperatures at which it is liquefied. Liquid air is then evaporated. Nitrogen and other constituents of air are vaporized at lower temperatures than oxygen which thus remains in the liquid state.

Gaseous oxygen is stored and transported under high pressure in steel

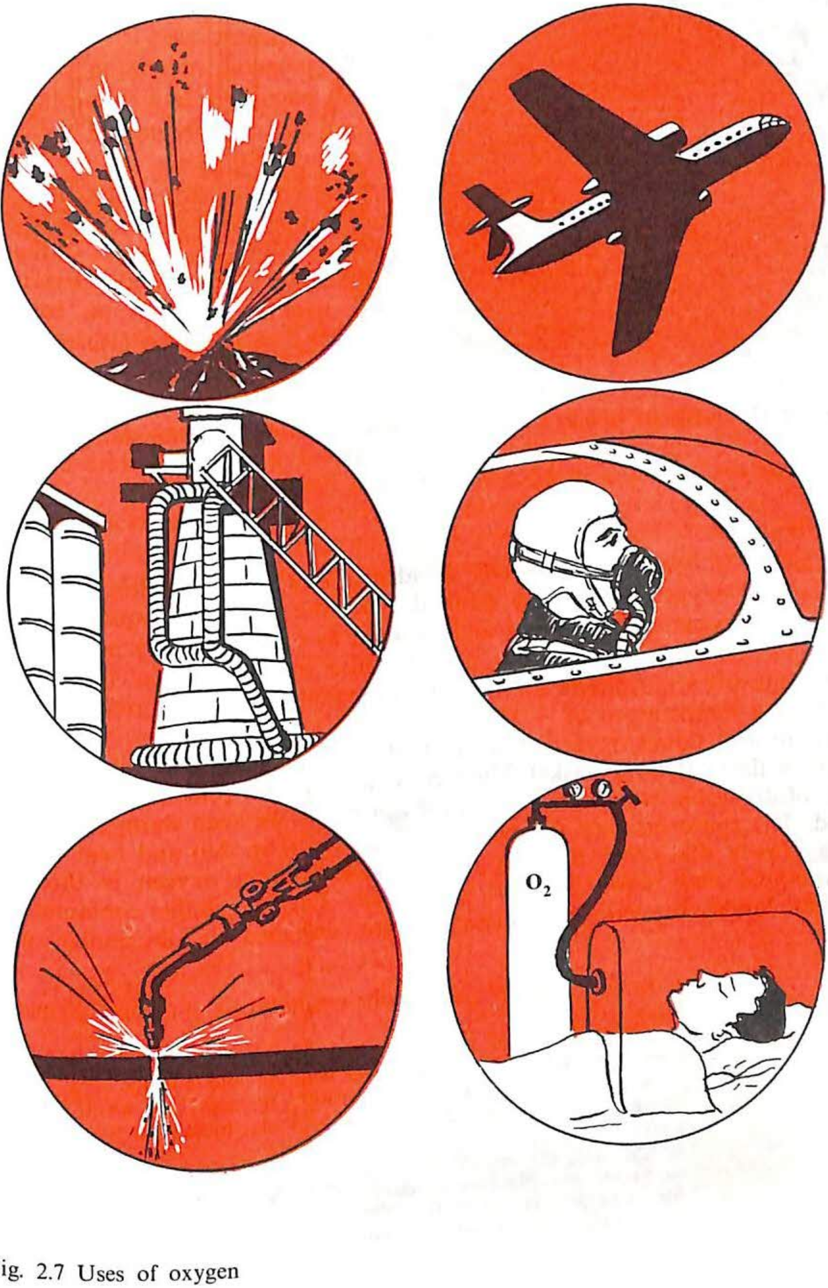

Fig. 2.7 Uses of oxygen

2.5 Uses of Oxygen

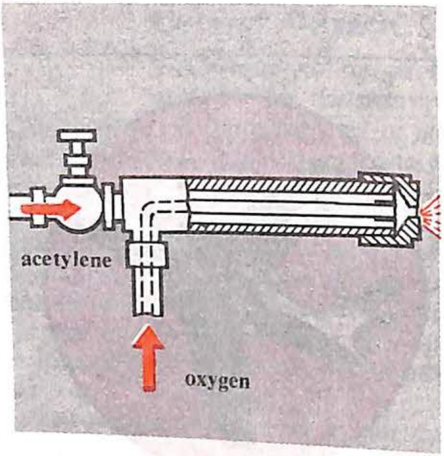

Fig. 2.8 Oxyacetylene torch

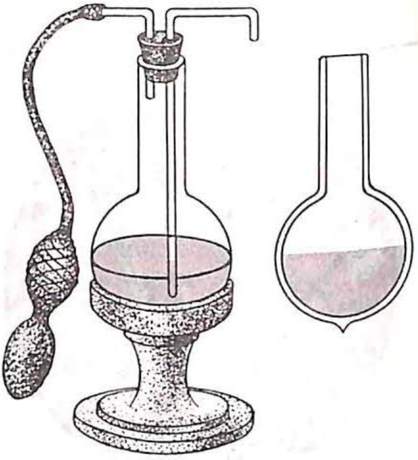

Fig. 2.9 Dewar flask for storage of liquid oxygen

cylinders. In order to prevent accidents due to confusion, cylinders containing oxygen are always painted blue (the colour of liquid oxygen).

Liquid oxygen can be stored and handled as well. It is only necessary to keep the container away from heat because even in winter (at subzero temperatures) atmospheric air is 'hot' compared with liquid oxygen which boils at a temperature of -183°C.

To protect liquid oxygen from heat of the surrounding air, it is kept in vacuum flasks (Dewar flasks). Their construction is in principle the same as that of domestic twinwall vacuum flasks in which we keep warm drinks and food. The space between the walls is evacuated (Fig. 2.9) and heat is thus very slowly dissipated through this obstacle. Liquid oxygen is therefore evaporated very slowly in such containers. Large metallic containers in which liquid oxygen is transported are designed in a similar way.

?
△

1. Look at Fig. 2.7 and describe practical uses of (a) gaseous and (b) liquid oxygen.
2. The formula of acetylene is C_2H_2. Write down equations of reactions that occur during steel welding and cutting.
3. A diver submerges with a burning oxyacetylene torch and the flame is not extinguished. Explain how can metals be welded under water.
4. Calculate the minimum weight of liquid oxygen that is necessary to ensure complete combustion of a given amount of coal. (When the components are mixed, the explosion is the strongest.)
5. Describe the industrial manufacture of oxygen.

2.6 Preparing Oxygen

In the laboratory oxygen is obtained by heating substances that readily decompose to liberate oxygen. These are, for example, potassium permanganate $KMnO_4$ (normally used in homes as a disinfectant) and hydrogen peroxide H_2O_2. When hydrogen peroxide is heated it decomposes to liberate oxygen and water

$$2H_2O_2 = 2H_2O + O_2 \uparrow$$

To accelerate the reaction, a pinch of black manganese(IV) oxide MnO_2 should be added to the hydrogen peroxide. The mixture formed can be easily separated. Water readily passes through a filter, while the black powder is retained on the filter surface. The precipitate on the filter is the same manganese(IV) oxide. It can be reused in the reaction to accelerate decomposition of another portion of hydrogen peroxide. The quantity of the manganese dioxide powder does not diminish during the reaction. Manganese dioxide MnO_2 thus accelerates the decomposition of hydrogen peroxide and is not spent in the reaction.

Substances that alter the rate of a chemical reaction but themselves remain unreacted are called catalysts.

Oxygen is slightly heavier than air and is sparingly soluble in water. It can therefore be collected in two ways: above water (Fig. 2.10), and by displacing

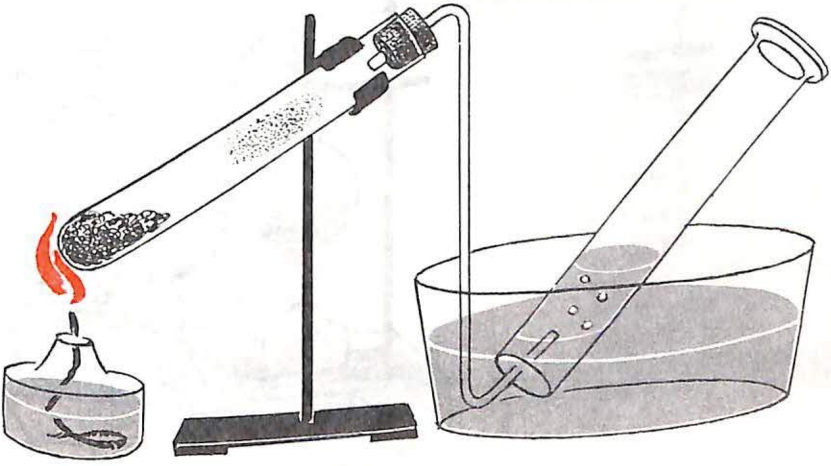

Fig. 2.10 Collecting gas above water

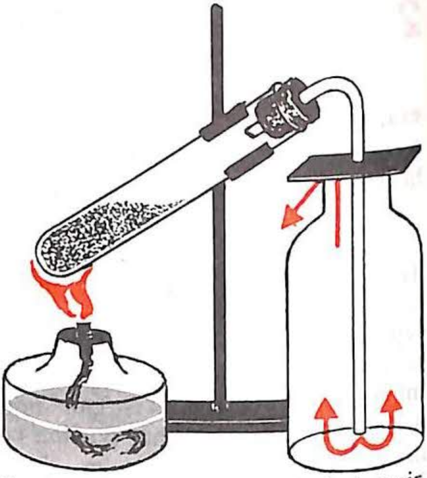

Fig. 2.11 Collecting gas by displacing air

air from a bottle (Fig. 2.11). In the former case oxygen displaces water from a vessel and in the latter it displaces air (as if oxygen were an invisible liquid). In order to make sure that the vessel is filled with oxygen, a glowing splint should be held to the mouth of the vessel. If oxygen fills the vessel to the top, the splint bursts into flame at the very mouth of the vessel. Oxygen in the laboratory is kept in a special apparatus shown in Fig. 2.12, from which it is dispensed for experiments.

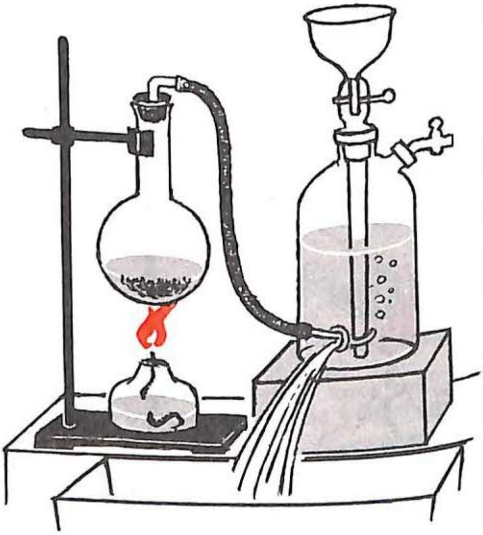

Fig. 2.12 Collecting gas in a gasometer

■ Try to set a lump of sugar on fire. Does it burn? Put a heap of ash or cinder over the lump and set on fire again. Describe your observations. What role does cinder play in this experiment if it is known not to burn nor to support burning?

2.7 The Composition of Air

The discovery of oxygen and the study of its properties opened the way to the study of the air composition.

Take a bell jar which we have already used for combustion of phosphorus in oxygen (Fig. 2.13). Mark the glass at the water level and divide the remaining volume of the bell into five equal portions. The bell jar contains air. Now put a lump of phosphorus in the spoon, ignite it, lower the spoon in the bell jar, and stopper it immediately. Wait till the fire extinguishes (part of phosphorus remains unburnt) and the bell jar cools. The water level in the bell jar has risen to the second mark to indicate that the volume of air in the bell jar has decreased by one fifth. This is the volume of oxygen that was spent to burn phosphorus. It means that the oxygen makes about 21% by volume, while the gases that do not react with phosphorus are about 79%, that is 4/5 of air.

Add water to the vessel to align its level with that in the bell jar. Remove the stopper from the bell jar and lower a burning candle into the bell jar. The flame of the candle is extinguished. Pour lime water into the bell jar: the gas in the jar does not make it cloudy. This indicates that the gas is not carbon dioxide. The gas does not support burning, or breathing. In contrast to carbon dioxide it does not act on lime water. The gas is nitrogen.

When air was studied in more detail it appeared that in addition to oxygen and nitrogen, it also contains five other gases which are known as

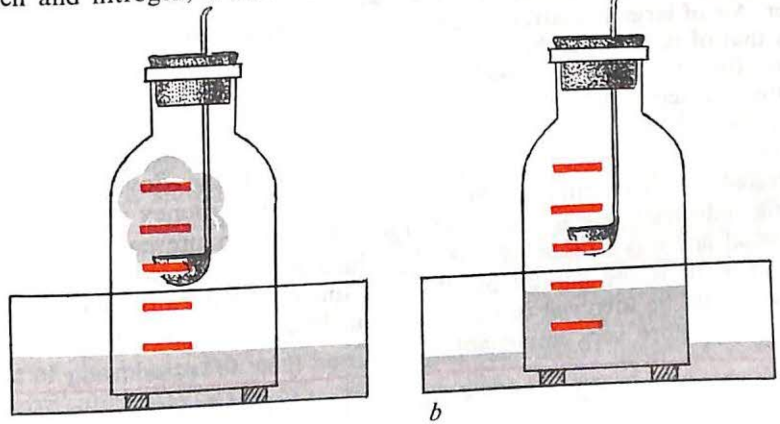

Fig. 2.13 Determining composition of air: *a*–apparatus before the experiment, and *b*–apparatus after the experiment

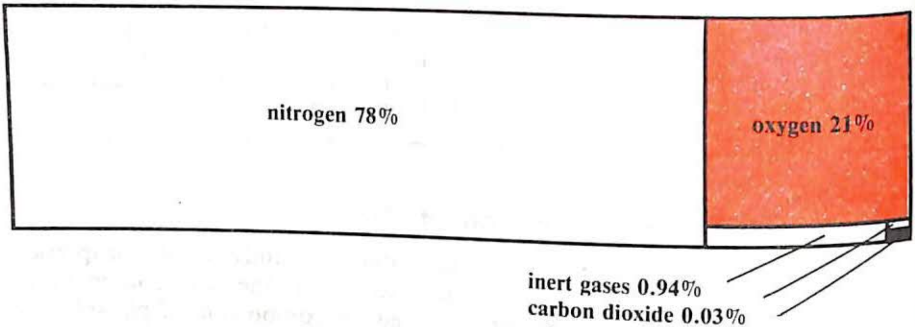

Fig. 2.14 Volumetric composition of air

noble or inert. These are argon Ar, neon Ne, krypton Kr, xenon Xe, and helium He. These gases make up about 1 per cent of air by volume (Fig. 2.14). The noble gases are monatomic, that is their molecules consist of one atom.

Argon, neon, krypton, xenon and helium are nonmetals. They form a special family of chemical elements known as *inert*. Unlike atoms of all other nonmetals, the atoms of inert elements: (1) do not combine with one another, (2) nor do they combine with hydrogen or metals.

It had been thought for a long time that the noble gases do not take part in chemical reactions at all (hence the name). It has recently been found that some compounds (oxides included) can be obtained that include inert elements of higher atomic weights.

In addition to the mentioned simple substances, air contains very small quantities of carbon dioxide (CO_2) and water vapour (H_2O). The amount of water vapour in the air varies depending on weather conditions: in warm and humid air, the content of water vapour is higher and in cold and dry, lower. Air of large industrial cities contains larger amounts of carbon dioxide than that of rural areas, because much fuel is burnt and many people live in them. But air streams (winds) agitate the air to level its composition.

Other gaseous substances may be present in the air over industrial enterprises. Some of them may be harmful to man, animals, and plants.

The natural wealth, and the environment of the Soviet Union are protected in this country by the Constitution. Much money is spent on purifying industrial wastes and discharges in order to prevent air pollution. A special law was adopted in 1980 by which air is protected from pollution. But since air is the habitat of all living on the Earth, all countries of the globe should be involved in its protection. International cooperation in this field is therefore very important.

?
△

1. What simple substances and compounds are contained in the air?
2. What is the composition of air (to an accuracy of 1 per cent)?
3. The composition of air was first established by the French investigator Antoine Lavoisier. He gently heated mercury in a definite volume of air to establish that the volume of air decreased,

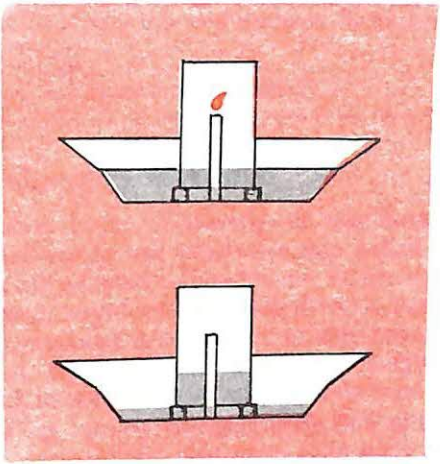

Fig. 2.15 Examination of air composition

while the mercury became covered with an orange film. The remaining gas did not support burning or breathing. Lavoisier collected the orange scales, placed them in a test tube, heated strongly, and collected the liberated gas. He then mixed the gas collected with the remaining gas of the initial air to restore the compostion of the air. Explain the experiment carried out by Lavoisier and write equations for the reactions which he used to establish the composition of air.

■ Prepare nitrogen as shown in Fig. 2.15. Examine its properties using a burning splint. For the purpose of comparison, put the burning candle in a beaker filled with air. If a candle is not available, be inventive and burn something else. Describe your experiment, and try to explain the phenomena observed.

2.8

Burning and Slow Oxidation

A reaction accompanied by liberation of heat and light is called burning.

Burning in air is slower than in oxygen because oxygen in air is diluted with nitrogen and a smaller number of oxygen molecules come in contact with the surface of burning substance than during burning in oxygen. The temperature of burning in air is lower than in oxygen because the heat liberated is spent not only to heat the products of combustion but also to heat the nitrogen in the air. Phosphorus burns in air and in oxygen to form the oxide of phosphorus (V); coal burns to give carbon (IV) oxide CO_2; sulphur to give sulphur (IV) oxide SO_2. When a knife is sharpened on a rotating emery stone, bright sparks fly into the air. The sparks are hot particles of the iron scale that is formed during steel burning in pure oxygen.

In order to set a combustible substance on fire, it should first be heated to a certain temperature, which is known as the *ignition point* of a substance.

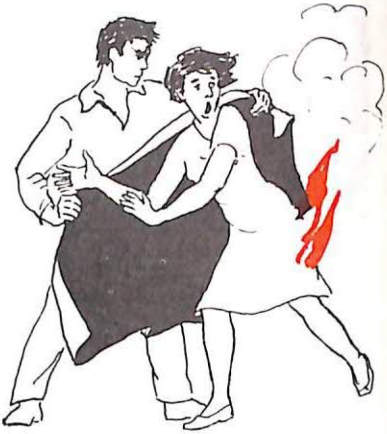

Fig. 2.16 Quenching fire

The ignition point of sulphur and wood is about 270°C and of coal, 350°C. If a free access of air to the burning substance is ensured, it continues burning because the heat liberated maintains the temperature above the ingition point of the substance. In other words, in order to ignite a substance, it is necessary (1) to heat the substance to a temperature at which it ignites, and (2) to ensure unobstructed access of oxygen to it.

And what is necessary to do the reverse, i.e. to stop burning? It is quite evident that one must either cool the burning substance to the temperature below its ignition point, or discontinue the access of oxygen to it.

Put a small amount of alcohol into an open dish and fire it. Now cover the dish with a sheet of dense paper and press tightly. Burning stops as soon as the delivery of oxygen is discontinued while the paper does not even catch fire because burning stops before the paper is heated to its ignition point.

Fire can thus be extinguished by covering the burning object with, for example, a blanket or some other cover at hand (Fig. 2.16). One must act firmly and promptly. Many lives have been saved and fires prevented by resolute and clever measures. In order to stop burning of wood or coal water may be used. Water cools the burning substance and separates it from contact with oxygen in the air.

Combustible substances may be oxidized with liberation of heat but without burning. The process is known as slow oxidation.

Manure, for example, is oxidized in air with liberation of heat and is therefore used to warm soil in hot-houses and greenhouses.

If the heat liberated is not withdrawn into the environment, the temperature of a slowly oxidizing substance may rise to its ignition point, i.e. self-ignition takes place. It is prohibited to keep oil-soaked rags in large heaps because spontaneous ignition may occur and cause a fire.

?
△

1. Why is the burning process slower in air and faster in oxygen? Why is the temperature of a flame higher in oxygen than in air?

2. What is necessary to ignite a substance and maintain its burning?
3. What is the ignition point?
4. How can burning be stopped?
5. What is slow oxidation and spontaneous ignition?

2.9

Uses of Air. Combustion of Fuels

Slow oxidation reactions occur incessantly in the human body. When we feel well we do not experience any deficit of oxygen. The lungs of the mammalians are adapted to breathe air, rather than pure oxygen as is the case with fish which breathe oxygen dissolved in water. In order to ensure adequate oxidation processes in our body we only have to air the room in due time so that the used air might be renewed.

The reaction of burning of combustible substances in air is widely used in industry and in homes. Materials that are burned for generation of heat are called *fuel*. Fuels may be solid, liquid, and gaseous. The main solid fuels are coal, peat, oil shales, and wood. Coal was formed in the depth of the Earth's crust from plant remains. The maximum heat is liberated when the oldest coal is burned. This is known as anthracite. Since peat and oil shales have much lower heating values, they are mainly used locally.

Petrol and kerosene are the main liquid fuels that are produced from petroleum.

Natural gas is widely used as gaseous fuel and the field of its application is ever widening. Gaseous fuel has many advantages over solid fuel: it burns leaving no ash, and the furnace for its combustion is very simple and easily adjustable. It may be brought from its natural deposit by pipes.

Figure 2.17*a* shows the simplest device–the furnace for combustion of solid fuel (such as wood or coal). Air is delivered to the furnace through an opening in the bottom (ashpit). In order to ensure rapid replacement of the gaseous combustion products by fresh air, blowers are used, or chimneys are attached to the furnace. Strongly heated gaseous combustion products give off their heat to water in boilers or to other heat-exchange media, and are released into the atmosphere through the chimney. A draught is thus provided by which fresh air is drawn into the furnace through the ashpit and the grates.

Let us now use our knowledge of the general laws underlying chemical reactions to explain the processes that occur in the furnace. In order to successfully control a chemical reaction, its operating principle should be known. The operating principle underlying the reaction of combustion in air is that of the interaction of a combustible material with oxygen.

Like all other substances, fuels combine in definite proportions with oxygen. The amount of air delivered into the furnace should therefore be sufficient to ensure complete combustion of the fuel. If the air supply is insufficient, part of the unreacted combustible material and carbon particles (carbon black) will be carried away from the furnace through the chimney. When carbon black particle are present in the smoke it becomes black. In order to ensure complete combustion of fuel we usually supply more air than

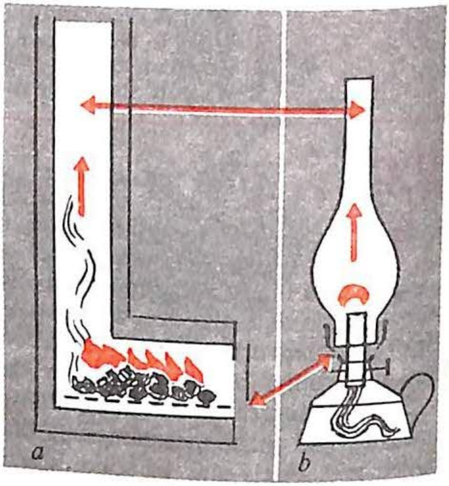

Fig. 2.17 Diagram of (*a*) furnace and (*b*) kerosene lamp

is necessary into the furnace. If the supply is too great, the complete combustion of fuel will be attained, but some of the heat liberated during the combustion process will be wasted to heat the excess air. Incorrect adjustment of the combustion process will thus become the source of great economic loss.

The design of industrial furnaces resembles in many respects that of stoves used in houses, the difference being that an industrial furnace would normally run on a continuous schedule due to continuous delivery of fuel on the grate.

Pulverized (powdered) fuel is burnt in the suspended state. It is blown into the furnace together with air or water vapour through a nozzle (Fig. 2.8) of an injector. Gaseous fuel is best of all mixed with air and complete combustion can thus be ensured.

Burning is the first chemical reaction that was controlled and mastered by man. When man learnt to produce fire, he was saved from cold in winter, and could now boil otherwise inedible seeds or roots of plants, and finally man learnt how to smelt iron from ores.

The energy liberated during combustion of fuel is used not only in the form of heat. At power stations heat is converted into electric current which is then used for industrial purposes, for illumination, etc. Combustion of liquid fuels (petrol, kerosene, etc.) in internal combustion engines is utilized to propel aircraft, cars, and other vehicles. Gaseous fuel is used for both industrial and domestic purposes.

Oxygen is consumed not only by man but by all living things. It might appear at first consideration that the store of oxygen in nature may thus be depleted over the years. But since the time when man learnt to determine the composition of air, the oxygen content of air has not changed appreciably. Botany teaches that the green plants absorb carbon dioxide from air and liberate oxygen (in the light). This is why the store of oxygen in nature does not diminish. The reversal of oxygen in nature is known as the cycle.

We have discussed the uses of air which are associated with the presence of oxygen in it. Let us now consider the other components of air.

The noble gases are now also widely used. Metals that are easily oxidized in air may be welded in argon. Krypton is used to fill electric bulbs. Since krypton does not affect the hot filament, the metal is not vaporized and the bulb has a longer life. Tubes filled with rarefied noble gases luminesce when electric current is passed through them. The colour of luminescence differs depending on a particular gas. Neon, for example, gives orange luminescence. Luminescent tubes are used for advertising purpose and as signal lamps. Light-houses equipped with neon lamps can be seen from a very long distance.

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△

1. A kerosene (oil) lamp (shown in Fig. 2.17,*b*) is the simplest furnace. What are the 'ashpit' and the chimney in this lamp? If the bulb is removed from the lamp the flame becomes smoky. Why? If we light an oil lamp with its wick in the lowermost position, and then lift gradually the wick, the flame will become gradually brighter until its brightness becomes maximum. If we continue raising the wick, the flame dulls and becomes smoky. Why? The same picture is observed if we block part of the lateral openings with a finger. Explain.
2. Take a candle and a length of a glass tube of about the same diameter as that of the candle, and try to repeat the experiments described above.
3. Describe the design of a furnace and its operating principle.
4. The chimney of an industrial enterprise emits black smoke. What does this indicate?
5. What are the uses of the reaction of burning (a) in industry, (b) in agriculture, (c) in cars, (d) in the home?
6. What are the uses of noble gases?

■

1. Name (a) the fuel used in your home, (b) devices that are used for combustion of this fuel. Establish if water is produced during combustion of the fuel.
2. Prepare a topic 'What I know about fuels used in industry, the methods by which they are burned, and the utilization of energy liberated during their combustion'.
3. Tell what you know about the oxygen cycle in nature and about control of air pollution.

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3 Hydrogen. Acids. Salts

Since acids first became known to man, the chemists noticed that if solutions of acids came into contact with some metals, 'combustible air' was liberated. If fire was applied to this 'air' it flared up or even exploded. The English scientist Henry Cavendish (who was a contemporary of Joseph Priestley) was the first to collect the 'combustible air' and to establish that this was not actually air but a gaseous substance. When the gas was pure it burned quietly, but when mixed with air it exploded. The gas was later given the name of hydrogen. Hydrogen is a simple substance whose molecules are formed by two atoms of the element of the same name.

3.1 Preparation of Hydrogen

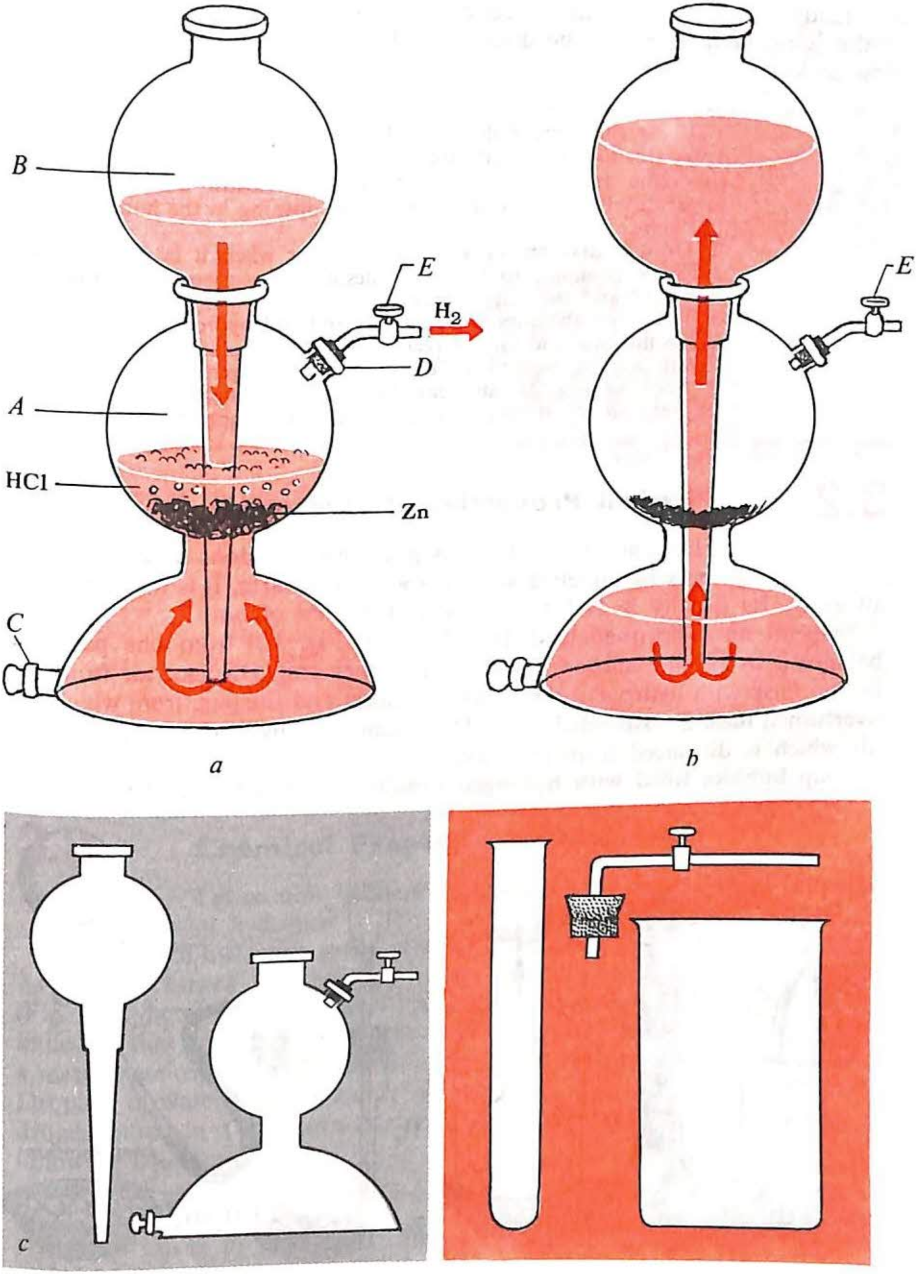
The chemical symbol of hydrogen is H, and atomic weight 1.008. The formula of hydrogen is H_2.

If pieces of zinc are placed in hydrochloric acid, gas bubbles are formed on the metal surface. The bubbles separate and rise to the acid surface. One has the impression that the liquid is boiling. The pieces of zinc soon dissolve completely, and a clear solution remains in the vessel. If we now evaporate it, a solid will precipitate. This is zinc chloride $ZnCl_2$. The reaction can be described by the following equation:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

Hydrogen is liberated from the acid due to its displacement by zinc. This explains the 'boiling' effect: the acid comes into contact with the surface of zinc to attack zinc atoms and to evolve hydrogen.

A Kipp gas generator is normally used in the laboratory to produce hydrogen. The apparatus is shown in Fig. 3.1. It consists of the upper bulb *B* and the central bulb *A* which is connected with the acid reservoir by a throat. When the upper bulb is inserted in the throat connecting the acid reservoir with the central bulb, its stem partly closes the throat so that zinc, which is placed in the central bulb through the tubulus *D*, does not fall into the acid reservoir. Acid is poured into the reservoir through the upper bulb *B*. As the acid rises to the central bulb it reacts with zinc to liberate hydrogen, which is withdrawn from the apparatus through a tube passed through a stopper that closes the tubulus *D*. When hydrogen is no longer required (the experiment is over) the stop-cock *E* is turned off. Hydrogen continues evolving but finds no outlet from the central bulb. It is thus coll
bulb to displace th


B
E
H_2
D
A
HCl
Zn
C
a
E
b
c

and ready to act. As soon as hydrogen is no longer required, the operation of the Kipp generator may be discontinued at any moment by closing the stop-cock *E*.

?
△

1. Using the objects shown in Fig. 3.2 one can assemble a simple apparatus for the manufacture of hydrogen. Its operating principle is the same as that of the Kipp generator. Draw a sketch of the apparatus. (Make sure that there is an opening in the bottom of the test tube.)
2. Draw a diagram of a Kipp generator when it is not working. What is common to both the design of a gasometer shown in Fig. 2.12 and the Kipp generator?
3. Place iron shavings in a test tube and add hydrochloric acid HCl. Write the equation for the reaction that takes place. Remember that $FeCl_2$ will be formed in addition to hydrogen in this reaction.
4. Look at Fig. 2.2 and calculate (approximately) the number of oxygen atoms that occur in nature per one hydrogen atom.

3.2 Physical Properties of Hydrogen

Hydrogen is a colourless gas, with no odour or taste. It can only be liquefied at very low temperatures. It is the lightest of all gases. Its density is 14.5 times lower than that of air.

Suspend an overturned flask (as shown in Fig. 3.3) from one pan and balance it by placing another flask on the other pan. Displace air from the former flask with hydrogen: the balance is upset and the pan, from which the overturned flask is suspended, rises. This means that hydrogen is lighter than air which is displaced from the flask.

Soap bubbles filled with hydrogen rapidly rise in air (Fig. 3.4).

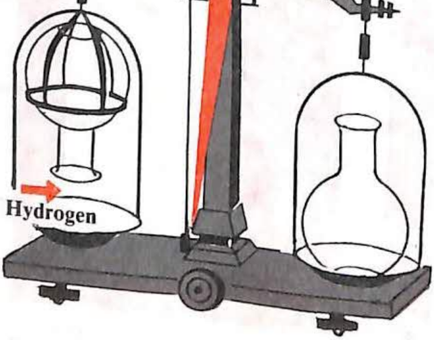


Fig. 3.3 Hydrogen is lighter than air

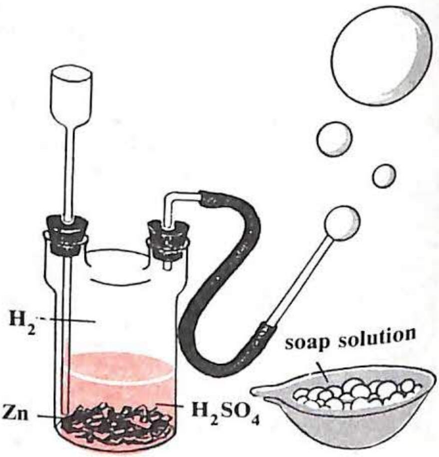


Fig. 3.4 Soap bubbles filled with hydrogen

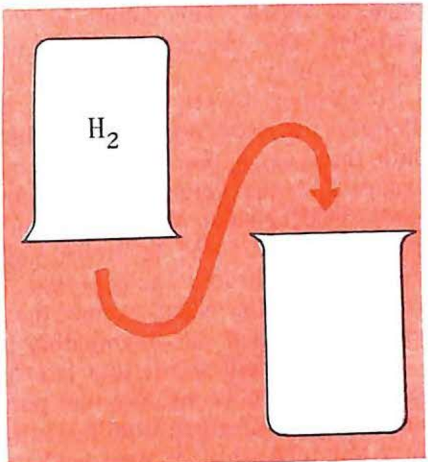


Fig. 3.5 Pouring hydrogen from one container to another

Hydrogen is sparingly soluble in water and it may therefore be collected by displacing water from a vessel.

?

1. What is the difference between the physical properties of hydrogen and oxygen?
2. How can hydrogen be transferred from one beaker into another (Fig. 3.5) by displacing air from the latter? How can the absence of hydrogen in the former and the presence of hydrogen in the latter beaker be proved?
3. How can hydrogen be collected in a vessel? What properties of hydrogen shall be utilized?

3.3 Chemical Properties of Hydrogen

Let us now become acquainted with the chemical properties of hydrogen.

Light a jet of hydrogen issuing from a tube (after a preliminary testing for its purity). Lower the burning torch into a vessel containing oxygen (Fig. 3.6): the walls of the vessel become coated with droplets of water. This indicates that hydrogen combines with oxygen to form water. Now hold a metal plate over a flame of burning hydrogen (in air, as shown in Fig. 3.7). Droplets of water soon condense on the plate. This also indicates that hydrogen burns in air to form water. The reaction can be described by the following equation:

$$2H_2 + O_2 = 2H_2O$$

Hydrogen burns to give water. Hence the name hydrogen, which means giving birth to water (from Greek *hydros* water and *genes* born).

Hydrogen burns with liberation of much heat. A hydrogen flame is nothing else but white-hot water vapour. It is not therefore visible if the tube from which hydrogen is discharged is of iron. If the tube is made of glass, the flame is yellow. The colour is given to the flame by vapourized glass particles. The characteristic chemical property of hydrogen is thus its combustibility.

If we want to set fire to hydrogen, we must take special precautions. Perform this experiment. Take a thick-walled cylinder and divide its volume into three equal portions. Fill two volumes with hydrogen (by displacing water) and one volume with oxygen. Wrap the cylinder in a towel and (without delay) put a burning splint to the mouth of the cylinder: a loud explosion is produced. Hydrogen has combined with oxygen instantaneously. Hence the explosion. The heat that was liberated during this reaction caused expansion of the water vapour that was formed during the reaction. This expansion caused the surrounding air to vibrate.

The experiment shows that hydrogen issuing from a generator may only be ignited when we are sure that pure hydrogen, rather than its mixture with air, is being discharged from the tube. To that end hydrogen is first collected in a test tube which is then held to the fire of a burner (in the overturned position as shown in Fig. 3.8). If the hydrogen is pure, it burns quietly with a slight puff. If the hydrogen contains air, the mixture explodes with a specific whistling sound. The explosion in the test tube is safe, but if a large vessel is taken (especially if its mouth is narrow) it will burst into pieces and the fragment may cause serious injuries to the surrounding people. We can thus conclude that a mixture of hydrogen with air or oxygen is explosive, and before applying a flame, we must test hydrogen for purity.

When hydrogen burns quietly or explodes in mixtures, one and the same reaction occurs: hydrogen combines with oxygen. When hydrogen burns in air the reaction is slow and gradual (new portions of air come gradually into contact with new portions of hydrogen). An explosion of a mixture of hy-

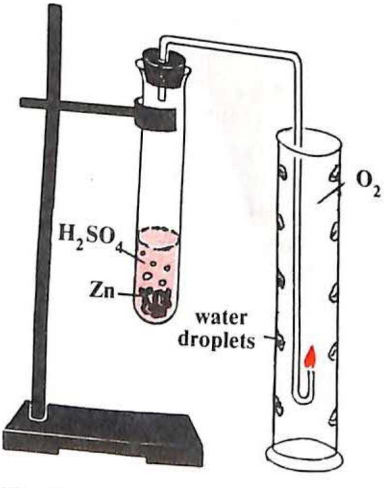


Fig. 3.6 Burning of hydrogen in oxygen

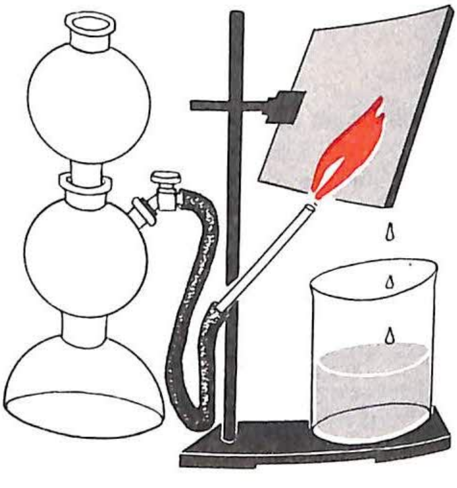


Fig. 3.7 Formation of water during hydrogen burning

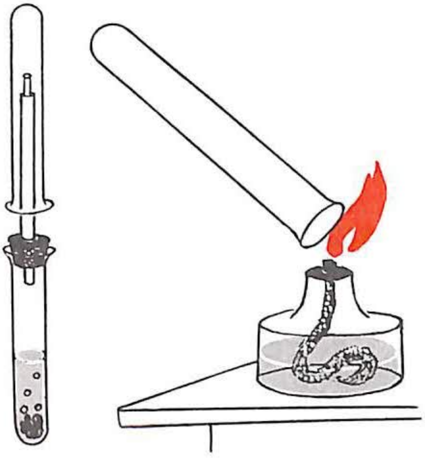


Fig. 3.8 Testing hydrogen for purity

drogen with air or oxygen is an instantaneous reaction because the molecules of the gases were mixed preliminarily.

Let us consider another chemical property of hydrogen. Place copper (II) oxide in a glass tube and pass a stream of hydrogen over it (Fig. 3.9). (The hydrogen should preliminarily be tested for purity!) No reaction occurs. Now heat the cupric oxide: the oxide becomes very hot, which indicates that a chemical reaction with liberation of heat has begun between cupric oxide and hydrogen. Water droplets precipitate on the tube walls, while the black

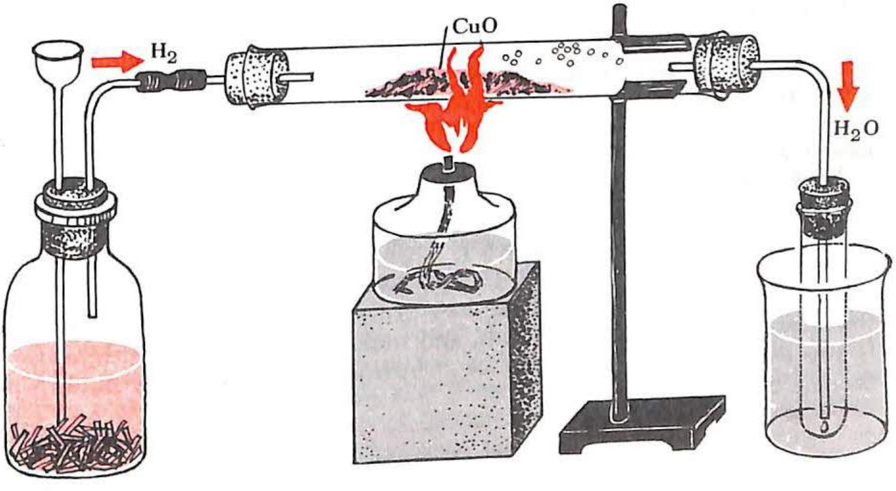


Fig. 3.9 Reduction of copper from copper(II) oxide using hydrogen

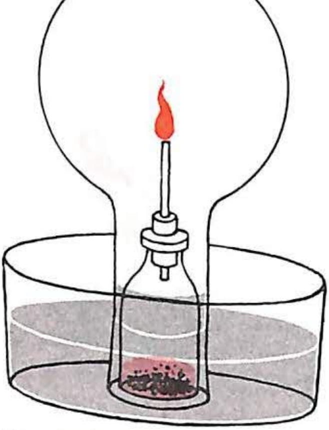


Fig. 3.10 Cavendish's experiment

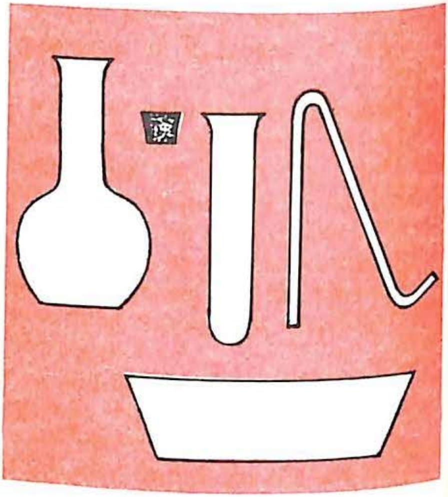


Fig. 3.11 Parts of the apparatus (the stopper has an opening to pass the tube)

cupric oxide becomes red. The red powder is metallic copper. The reaction is as follows:

$$CuO + H_2 = Cu + H_2O$$

Hydrogen has taken oxygen from the cupric oxide and combined with it to form water and *reduce* copper.

It can be concluded that hydrogen can not only combine with free oxygen but also take it from other compounds. This is another important chemical property of hydrogen. Tungsten, the metal from which filaments for electric bulbs are manufactured, is produced by this method.

Substances that can take oxygen from other substances are known as reductants (reducing agents).

As we can conclude, hydrogen is such a reducing agent.

Its light weight and the ability to reduce other substances account for the many uses of hydrogen. Hydrogen is used to fill balloons that are used for high-altitude research. Some very important metals are reduced from their oxides by hydrogen. Hydrogen is used as the chemical starting material in the manufacture of ammonia, acids, and some organic substances. Hydrogen is also used as fuel. The importance of hydrogen as a fuel in the future will become even greater.

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△

1. Describe the chemical properties of hydrogen.
2. Describe the reaction of copper reduction from cupric oxide. What substances are called reductants?
3. Write the equations for reactions of hydrogen with the following oxides: (a) tungsten oxide WO_3, (b) iron scale, (c) mercury(II) oxide.

What chemical property of hydrogen underlies these reactions? What kind of reactions are these?

4. Take a copper plate. How can it be turned chemically into copper powder? Write equations for the appropriate reactions.

5. H. Cavendish performed the following experiment. He put acid and metal in a flask, placed the flask in water, fired the issuing gas, and covered the flask with another, larger flask as shown in Fig. 3.10. Describe the phenomena that Cavendish observed subsequently, if we know that hydrogen cannot combine with nitrogen in these conditions.

6. Three flasks are filled with gases: air, hydrogen and oxygen. How can the gases be identified?

7. Look at the objects shown in Fig. 3.11. How can they be assembled into an apparatus for proving that oxygen is consumed during hydrogen burning in oxygen? Draw a sketch of this apparatus and describe the procedure of the experiment.

8. Describe the uses of hydrogen that you know.

3.4 Hydrogen in Nature. Acids

Hydrogen is part of one of the most abundant substances, water. It is therefore an abundant element as well. Hydrogen is also a constituent of the complicated substances from which living organisms are made. Acids are among substances that contain hydrogen. Many acids occur in nature. These are citric acid (contained in lemons), malic acid (apples), oxalic acid (sorrel), etc. Ants produce formic acid which they use to fight their enemies. Formic acid is also contained in nettle and bee stings. As grape juice becomes sour, vinegar is produced that contains acetic acid. Sour milk contains lactic acid, which is also contained in sour cabbage, etc. Apart from naturally occurring acids, acids produced by man are also known. Sulphuric and hydrochloric acids are among the most important artificially produced acids.

Sulphuric acid H_2SO_4. This is a collourless oily liquid without odour, almost two times heavier than water. Sulphuric acid absorbs moisture from air and other gases. Because of this property it is used to dry gases (which are passed through the acid).

When sulphuric acid is mixed with water much heat is liberated. If water is added to the acid, it will boil without even being mixed with the acid, and splashes of the liquid will injure the hands and the face of an inexperienced worker. Sulphuric acid must therefore never be diluted by adding water to it. If the acid has to be diluted it should be poured in a thin stream into the water with agitation of the vessel. Never should water be added to the acid!

Sulphuric acid chars wood, skin, and fabrics. If we immerse a splint in sulphuric acid, wood blackens due to a chemical reaction by which carbon is isolated from wood in the form of charcoal. Hence the danger of sulphuric acid coming into contact with the skin or clothes.

Hydrochloric acid HCl. This is an aqueous solution of hydrogen chloride gas, and unless strongly diluted, it smells of this gas. The odour is pungent. Hydrogen chloride gas combines with water vapour contained in air.

A specific mist is formed above the surface of hydrochloric acid. The acid is said to 'fume'.

General Properties of Acids. We shall use hydrochloric and sulphuric acid to establish some properties that are common to all acids.

Add a few drops of violet litmus solution to solutions of both acids: the litmus colour changes from violet to red. Another stain, methyl orange, turns pink when mixed with the acids. Litmus and methyl orange are *indicators* which are used to establish the presence of acid in solutions.

Drop pieces of zinc, iron, magnesium, and copper into both solutions. Zinc, magnesium, and iron displace hydrogen from both sulphuric and hydrochloric acids. (Identify hydrogen by firing it.) The reaction of the acids with magnesium is especially rapid. The reaction with zinc is slower, and the slowest is the reaction with iron. No changes are observed in test tubes containing copper. This means that the ability to displace hydrogen from acids is different for various metals. Some metals do not displace hydrogen from acids at all. There exists a special electrochemical series of metals from which one can establish if a given metal will or will not displace hydrogen from acid (the electrochemical series will be discussed later).

$$\underbrace{\text{K Na Mg Al Zn Fe Ni Sn Pb}}_{\text{displace hydrogen}} \qquad (H_2) \qquad \underbrace{\text{Cu Hg Ag Pt Au}}_{\text{do not displace hydrogen}}$$

The series begins with the alkali metals and ends with gold. All metals that come before hydrogen in the series displace it from acids, their displacing power decreasing from potassium to lead, while the metals that come after hydrogen do not displace it.

We used the reaction of zinc with hydrochloric acid to prepare hydrogen. The atoms of zinc (a divalent metal) displaced two hydrogen atoms in the molecules of hydrochloric acid, and zinc chloride $ZnCl_2$ was thus produced. Since the molecule of the acid contains only one hydrogen atom, two molecules react with a zinc atom (see equation on page 62).

Hydrogen may be obtained from other acids as well; for example, from sulphuric acid. The reaction between zinc and sulphuric acid is as follows:

$$Zn + H_2SO_4 = ZnSO_4 + H_2\uparrow$$

In this case, two hydrogen atoms are again displaced by one zinc atom.

The common properties of acids are therefore the following:

(1) Acid solutions taste sour (Latin *acidus* means sour). This property of acids is known to us from everyday experience.

(2) Acid solutions change the colour of litmus to red and of methyl orange to pink. Litmus is more sensitive to acids than our tongue and can detect them in very dilute solutions when our tongue fails to taste any sourness.

(3) Almost all acids liberate hydrogen when acted on some metals.

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△

1. What rule should be followed in diluting sulphuric acid?
2. What general acid properties do you know? Illustrate your answer by examples.

3. Will a reaction occur if sulphuric acid is added to mercury? Explain your answer.

4. How can the presence of hydrogen in hydrochloric acid be proved experimentally?

Obtain from the laboratory assistant a few pieces of litmus paper (paper impregnated with litmus) and use them to prove the presence of an acid in foods that in your opinion may contain it, e. g. apple juice, sour milk, etc. Using litmus paper you can prove that milk is sour before it actually begins coagulating.

3.5 Composition of Acids. Salts

General properties of acids depend on the common features that are inherent in the composition of all acids. Look at Table 3.1 to compare the composition of various acids. A molecule of any acid contains hydrogen atoms. Moreover, each molecule contains atoms or groups of atoms that are known as the *acid residue.*

Acid is a compound each molecule of which contains one or more hydrogen atoms, that can be substituted by metal atoms, and an acid residue.

Table 3.1

Acid	Formula	Acid residue
Hydrochloric acid	HCl	$\overset{I}{Cl}$
Nitric acid	HNO_3	$\overset{I}{NO_3}$
Sulphuric acid	H_2SO_4	$\overset{II}{SO_4}$
Phosphoric acid	H_3PO_4	$\overset{III}{PO_4}$

Valency is the property inherent not only in an atom but in a group of atoms as well, for example in an acid residue. If an acid residue is connected in an acid molecule with one hydrogen atom, it is univalent; if with two hydrogen atoms, divalent, if with three hydrogens, tervalent, etc. The valency of acid residues in the Table above is indicated by Roman numerals.

When hydrogen is displaced from acids by metals, the acid residues remain intact and become part of a new compound, that are known as salts.

A salt is a compound in which metal atoms are bonded with the acid residue.

Formulas of salts are made out like those of binary compounds once the valency of the metal and the acid residue are known. Let us write the formula of, for example, aluminium sulphate, once it is known that aluminium is tervalent. Act as follows:

(1) Write the chemical symbols of aluminium and the residue of sulphuric acid, and superscribe their valencies in Roman numerals:

$$\overset{\mathrm{III}}{\mathrm{Al}} \qquad \overset{\mathrm{II}}{\mathrm{SO_4}}$$

(2) Find the least common multiple of the valencies of the acid residue and aluminium. This is 6.

(3) Determine the number of aluminium atoms and of acid residues in the molecule of the salt. To do this divide the least multiple 6 by the valency of aluminium $6:3=2$. It means that each molecule of the salt contains two aluminium atoms. Now divide the least common multiple by the valency of the acid residue $6:2=3$. This means that the salt molecule contains three acid residues.

The formula of aluminium sulphate is this $Al_2(SO_4)_3$.

Names of salts are formed from the name of the metal followed by the stem of the nonmetal's name with an added appropriate suffix. For example, NaCl is sodium chloride. The first name is that of the metal sodium, and the second word is the combination of the stem of the name of chlorine 'chlor' plus the suffix *-ide* (see Table 3.2).

Table 3.2

Nomenclature of Salts

Acid		Salt
Name	Chemical formula	
Hydrofluoric acid	HF	fluoride
Hydrochloric acid	HCl	chloride
Hydrobromic acid	HBr	bromide
Hydriodic acid	HI	iodide
Sulphuric acid	H_2SO_4	sulphate
Sulphurous acid	H_2SO_3	sulphite
Hydrosulphuric acid	H_2S	sulphide
Nitrous acid	HNO_2	nitrite
Nitric acid	HNO_3	nitrate
Phosphoric acid	H_3PO_4	phosphate
Carbonic acid	H_2CO_3	carbonate
Silicic acid	H_2SiO_3	silicate

But the metal involved may exhibit more than one valency. The use of Roman numerals (which follow in parentheses the name of metal) help differentiate between different salts. For example iron may exhibit valency II and III and form two salts: ferrous chloride $FeCl_2$ and ferric chloride $FeCl_3$, which will then be written iron(II) chloride and iron(III) chloride respectively.

? △

1. Write the formulas for the following salts: calcium chloride, potassium nitrate, calcium phosphate, iron(III) chloride, magnesium nitrate, sodium sulphate, iron(II) phosphate, and iron(III) phosphate.
2. Write the names of the following salts: (a) KCl, K_2SO_4, KNO_3, KI, K_2CO_3; (b) K_2S, K_3PO_4, KBr, K_2SiO_3, K_2SO_3.

3. Write the formulas for the following salts: (a) aluminium sulphate, sodium sulphite, barium nitrate, iron(III) nitrate, magnesium phosphate, magnesium iodide; (b) sodium bromide, sodium phosphate, lead(II) sulphate, potassium silicate, copper(II) nitrate, calcium chloride.

4. Write out separately the formulas of (a) oxides, (b) acids and (c) salts from the following: HNO_3, KNO_3, NO_2, SO_3, H_2SO_4, $CaSO_4$, K_3PO_4, H_3PO_4, Na_2O, CaO, $FeCl_2$. Name the compounds.

3.6 Action of Acids on Metal Oxides. Exchange Reactions

Not all salts can be obtained by the reaction between a given metal and the appropriate acid. You may remember that when pieces of copper were dropped in sulphuric acid, no reaction occurred. Copper does not displace hydrogen from sulphuric acid. How can salts of these metals, for example, $CuCl_2$, $CuSO_4$ be then obtained? Salts of metals that do not react with acids are obtained by chemical reactions of other types, for example, by the action of acids on metal oxides. Consider the reaction between an acid with a metal oxide, using copper(II) oxide and sulphuric acid by way of illustration.

Copper(II) oxide CuO is already known to us. This is a black powder. Put copper oxide in a test tube filled with water: it does not dissolve. Place another portion of the black powder CuO into another test tube and add sulphuric acid. Heat the mixture over a burner: a blue solution is obtained. Copper sulphate $CuSO_4$ may be obtained from this solution by evaporation. The reaction between copper(II) oxide and sulphuric acid is expressed by the following equation:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

We have thus become acquainted with another property of all acids: *they can react with metal oxides to form the corresponding salt and water*. As in the reaction of acids with metals, the acid residues remain unchanged and pass from the acid to the salt. Water molecules are formed from the oxygen atoms contained in the metal oxide and the hydrogen of the acid. Once we know this, we can write the equation of the chemical reaction between any acid and any metal oxide if the formulas of the oxide and of the acid are known to us. The coefficients should be so calculated that two hydrogen atoms would be provided by the acid for one oxygen atom in the oxide. It is unnecessary to select coefficients in the reaction between copper(II) oxide and sulphuric acid

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

because the two hydrogen atoms of the acid require one oxygen atom of the oxide.

Let us write the equation for the reaction between iron(III) oxide and nitric acid:

$$Fe_2O_3 + 6HNO_3 = 2Fe(NO_3)_3 + 3H_2O$$

Three oxygen atoms of iron(III) oxide and six hydrogens of the acid make three molecules of water.

Two compounds, namely metal oxides and acids, react to exchange their component parts: the oxides exchange their oxygen for acid residues, while acids exchange their hydrogen for metal atoms. This new type of chemical reaction is called an exchange reaction.

Exchange reactions occur between two compounds during which they exchange their component parts.

?
△

1. Write down equations for the following reactions:

(1) $ZnO + HNO_3 \rightarrow$
(2) $Al_2O_3 + HCl \rightarrow$
(3) $Na_2O + H_2SO_4 \rightarrow$
(4) $MgO + HNO_3 \rightarrow$

Give names to the salts obtained in these reactions.

2. What four types of chemical reactions do you know? What type of reaction is: (a) oxidation of simple substances by oxygen, (b) reduction of metals from their oxides by hydrogen, (c) displacement of hydrogen from acids by metals, (d) reactions between acids and metal oxides, (e) obtaining oxygen from hydrogen peroxide. Give one example for each reaction.

3. We dealt with copper(II) oxide in various chemical reactions. Describe this oxide according to the following scheme: (1) method of preparation, (2) class of compounds to which it may belong, (3) physical properties, (4) chemical properties, and (5) give equations for reactions by which copper(II) oxide is obtained or in which it is involved, and indicate the type of each reaction.

4. Describe the properties of sulphuric acid according to the following scheme: (1) composition; (2) physical properties; (3) chemical properties: (a) reaction with litmus, (b) reaction with metals, (c) reaction with metal oxides.

5. List the general properties of acids. Give examples of chemical reactions.

6. The following substances are given: magnesium, copper, copper(II) oxide, magnesium oxide, and hydrochloric acid. What experiments can be performed with these substances? Write equations for possible reactions. Specify conditions for their successful completion. Give names to the substances obtained by these reactions.

7. What is the composition of the atmosphere of a hypothetical planet if it is known that (a) oxygen burns in it; (b) wood and hydrogen do not burn; (c) when a beam of light is condensed on a piece of malachite through a magnifying glass, the mineral turns into a red powder (not black); (d) a meteorological balloon filled with hydrogen does not rise in this atmosphere? Write equations for the mentioned reactions.

8. Take pieces of coloured fabrics, and flowers (forget-me-not, lungwort, etc.). Try to establish which of them are coloured by substances that may be called indicators. Expain the change in colour of some flowers when they blossom.

4

Water. Solutions. Bases

4.1

Water in Nature. Obtaining Pure Water. Physical Properties of Water

The oxide of hydrogen, water (H_2O) is the most abundant and essential hydrogen compound in nature. It is found everywhere on the earth in its various forms. Water fills depressions of the Earth's crust to form lakes, seas and oceans. It covers about 75 per cent of the Earth's surface. Immense accumulations of ice and snow cover the polar regions of the globe and peaks of high mountains. The invisible vapour of water is always present in air. In the form of minute droplets water forms clouds that precipitate as rain to soak the soil and to feed springs, streams, and rivers. As atmospheric precipitation (rain) passes through the soil it dissolves some of its components and carries away some insoluble solids. Natural water therefore contains admixtures of many other substances.

Depending on its use, these impurities should be separated from untreated water to a greater or lesser degree. Purification of potable (drinking) water is especially important. Where does man take water for drinking? What impurities should not be contained in potable water?

Water taken from very deep wells hardly contains any suspended impurities or microorganisms. Such water contains dissolved salts that are useful to man.

Water supply systems of cities are fed from rivers or other water basins. River water contains many harmful impurities such as remains of animal and human life activity, and also pathogenic microorganisms. River water is first passed through filters which separate larger objects that float on the surface of water. Water is then allowed to settle in special tanks and passed through a bed of sand where insoluble solids are retained. Thus cleaned water is then treated with gaseous chlorine to kill pathogenic microorganisms that may remain in water. (Now the chlorine treatment is often replaced by exposure to the light of bactericidal lamps which kill microorganisms by ultraviolet radiation.) The incidence of infectious diseases has sharply decreased since potable water has been purified at water treatment plants. Potable water now contains only dissolved substances that are necessary to man. It is only in pharmacies that these dissolved impurities are separated from water before drugs are prepared. Pure water is also used in chemical laboratories. Pure water is prepared by separating dissolved impurities from it by distillation, during which water is converted into vapour by heating and then cooled (condensed) into liquid again. A simple apparatus used for water distillation in a laboratory is shown in Fig. 4.1. It consists of three main parts: a still (flask) where water is boiled, a cooler (condenser) where water vapour is condensed into liquid water, and a receptacle where purified water is collected. The condenser consists of two concentrically arranged tubes (a tube within a tube). The water vapour passes along the smaller inner tube, while cooling water is circulated in the larger outer tube in the direction indicated by the arrows. The circulating water cools the inner tube. When water is boiled in the still (flask) the dissolved substances remain in the liquid and only pure water vapour rises to pass the condenser from where it is collected in the receptacle. Water thus obtained is called distilled.

Large amounts of distilled water are prepared in an apparatus shown in Fig. 4.2. This differs from the apparatus shown in Fig. 4.1 in that it is manufactured from metals and not from glass, while the long tube through which water vapour passes is coiled so that it occupies smaller space in the condenser.

A similar process of water distillation occurs constantly in nature. Evaporated slowly by the heat of the sun, water rises from the ground to form clouds. Atmospheric precipitation (rain) is thus the purest natural water.

Water is a mobile colourless liquid (but bluish in large quantities) without odour or taste. It boils at 100 °C (under normal atmospheric pressure of 101.3 kPa, or 760 mmHg) and freezes at 0 °C. Its density at 4 °C is 1000 kg/m^3, or 1 kg/litre.

Water is a substance without which life on earth would be impossible. Human activities are also closely dependent on water. The demand for water is ever increasing with the development of industry and the well-being of man. The protection of natural water resources against pollution is therefore a very important problem. Projects are being undertaken by which industrial wastes will not be discharged into natural water basins. The dissolved

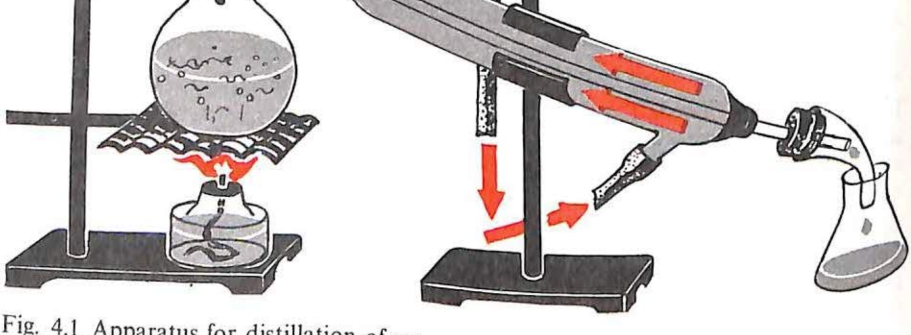

Fig. 4.1 Apparatus for distillation of water

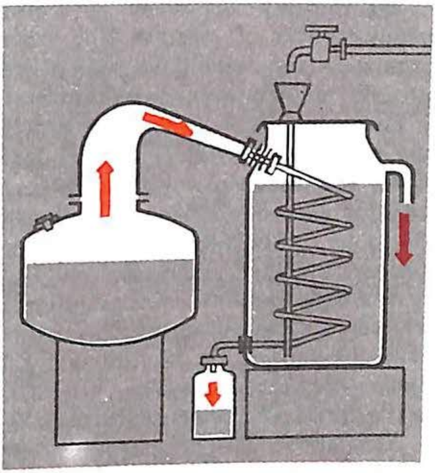

Fig. 4.2 Distillation vat

impurities will be separated from liquid wastes and the water thus recovered can be reused for industrial purposes.

According to the Constitution of the Soviet Union each citizen should protect nature and preserve natural resources.

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△

1. Which untreated water contains lesser amounts of impurities: water from springs or river water? Give reasons to your answer.
2. How is potable water purified?
3. For what purposes is water purified by distillation? Draw a sketch of an apparatus used for water distillation and name each component part of this apparatus. Describe its operating principle.

4.2

Water as Solvent. Solubility

From everyday experience we know that water can dissolve many substances, liquid, solid, and gaseous. In our chemical experiments we dealt with solutions of acids and alkalis. Since we have certain knowledge of the structure and composition of substances we can now try to clarify the essence of the dissolution process and to define *solution*.

We already know that molecules of substances are found to be in constant motion. This accounts for the phenomenon known as *diffusion* which is actually the distribution of one substance within another. Put a few crystals of blue vitriol in water in a glass cylinder and observe: after a certain time the water in the vicinity of the crystals turns blue. The invisible particles of blue vitriol have separated from the crystals and are carried about by water molecules. They have *diffused* in water. Diffusion is a slow process, but a uniformly homogeneous solution is eventually obtained.

The dissolution process can be speeded up if a powdered substance is taken instead of crystals. The surface of contact between the powdered substance and the liquid markedly increases and it dissolves sooner. The process may be even more accelerated if the liquid is agitated or heated.

Dissolution may also be accelerated by placing the *solute* on the surface of the solvent (Fig. 4.3). Since the density of solution is higher than that of water the dissolved substance tends to sink, as will be seen from Fig. 4.3: crystals in a bag of loose fabric dissolve and the solution formed 'flows' down to the bottom of the vessel in the form of streams. The dissolution process is thus accelerated.

The latter method of dissolution is used in industry. Lumps of salt are placed in a calico bag which is suspended in the upper portion of a barrel with the solvent. Or else salts are placed on a special grating in dissolution tanks. As will be seen from Fig. 4.4 the solution in such a tank will never settle but will on the contrary be always homogeneous.

Substances that do not dissolve in water, e. g. clay or chalk, remain suspended in water for a certain time and make the water cloudy but as time passes the suspended particles *precipitate* to the bottom of the vessel.

The solubility of substances is known to be limited. For example, 100 ml of water at 20 °C will only dissolve: 200 g of sugar, 35.9 g of sodium chloride, 20.7 g of copper sulphate or 0.2 g of calcium sulphate, etc. **A solution in which a given substance does not dissolve any longer at a given temperature is called saturated, while a solution which will further dissolve a given substance, is an unsaturated solution. The ratio of the weight of a substance that forms a saturated solution at a given temperature to a given volume of solvent is known as the solubility of this substance or a solubility coefficient.**

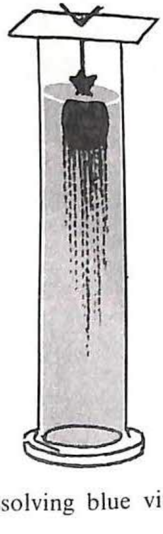

Fig. 4.3 Dissolving blue vitriol in water

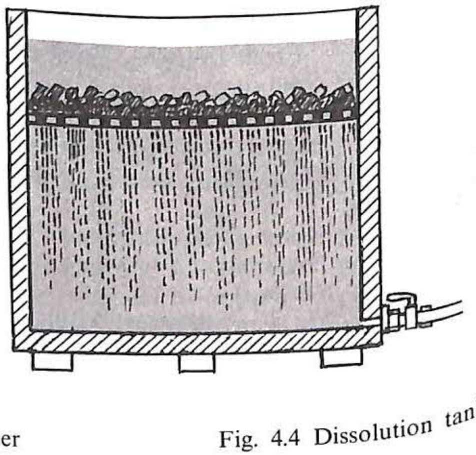

Fig. 4.4 Dissolution tank

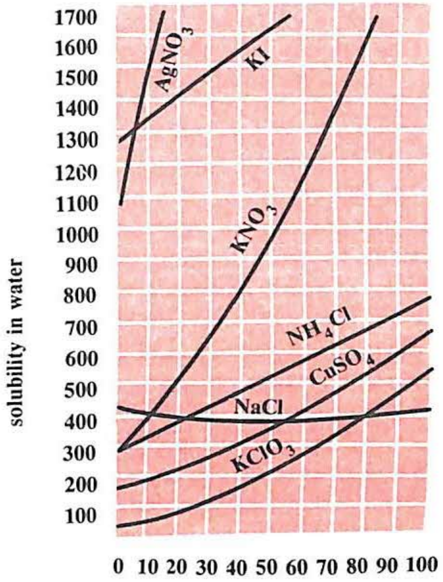

Fig. 4.5 Solubility of some salts

Solubility of substances varies within a wide range. For some substances solubility is so small that these substances can be practically regarded as insoluble. The solubility of barium sulphate $BaSO_4$ in water at 20 °C, for example, is as low as 0.0023 g/litre, and that of silver chloride AgCl, 0.0015 g/litre.

Does the solubility of a substance depend on temperature?

Prepare solutions saturated at normal temperature of potassium nitrate and sodium chloride in equal volumes of water. Now heat both solutions, and add new portions of the salts until they will no longer dissolve. We have thus prepared solutions that are saturated at temperatures close to boiling points. We have also established that the amounts of the salts that we have added are different. The solubility of potassium nitrate increases with heating to a greater extent than the solubility of sodium chloride.

Now allow the solutions to cool: crystals will soon start precipitating from the solutions. The amount of potassium nitrate precipitate will be markedly greater than that of sodium chloride.

The solubility of potassium nitrate will decrease with lowering temperature to a greater degree than the solubility of sodium chloride.

Changes in the solubility of some salts are vividly shown by the graph in Fig. 4.5.

The solubility of a very few substances decreases with increasing temperature. These are, for example, calcium sulphate, and calcium hydroxide.

Water dissolves certain liquids as well, for example, alcohol and glycerol. But petrol or vegetable oil are almost insoluble in water.

Some gases, e.g. oxygen, nitrogen, or carbon dioxide, are also soluble in water. This can easily be shown by placing a cup of cold water on a table in a room. After some time gas bubbles will be seen on the inner walls of the glass, which then separate from the walls and gather on the surface of the water. If water is carbonated this phenomenon is more striking. Carbonated drinks are solutions of carbon dioxide. A bottle of mineral water contains carbon dioxide dissolved in water under high pressure. When the bottle is opened, the pressure in the bottle drops and the dissolved gas evolves energetically to cause foaming of the water.

Solubility of gases increases with decreasing temperature and increasing pressure.

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△

1. How can the molecular theory be applied to explain dissolution of sugar in water?
2. How can dissolution of a solid substance in water be accelerated?
3. What is solubility, a saturated solution, an unsaturated solution?
4. How does solubility of solids change with increasing temperature? How does solubility of gases change with increasing temperature and pressure?
5. Why shouldn't boiled water be used in an aquarium?
6. A solution saturated at 10 °C and weighing 310 g contains 60 g of potassium nitrate. Calculate the solubility of potassium nitrate at 10 °C.
7. What amount of sodium chloride does a solution saturated at 20 °C and weighing 1 kg contain?

4.3 Determining the Weight Fraction of the Solute. Concentration

When using solutions it is very important to know the weight of solute contained in a given solution.

The ratio of the weight of solute to the total weight of solution is called the weight fraction of the solute or the concentation.

This is normally expressed in fractions of unity or in percentages (0.01 or 1%).

Consider, for example, two solutions of sodium chloride weighing 100 g. One of them contains 5 g of sodium chloride, the other 20 g. The weight fraction of the salt in the former solution is 5 g : 100 g = 0.05 or 5 per cent, while in the latter solution 20 g : 100 g = 0.20 or 20 per cent.

If the weight fraction of solute, for example of sulphuric acid in water is 10 per cent (a 10 per cent solution), this means that 100 g of aqueous solution of sulphuric acid contains 10 g of the acid and 100 g − 10 g = 90 g of water.

Solubility of substances should not be mistaken for the weight fraction of a dissolved substance (solute). Solubility of a substance shows the number of grams of solute that can be dissolved in 1 litre of water. The unit of solubility is gram per litre (g/litre). Concentration of solute indicates the fraction of solute in the total weight of solution. It can only be expressed numerically.

How can a 6 per cent solution of sodium chloride be prepared if its weight should be 250 g?

First determine the weight of the salt: $250\ \text{g} \times 0.06\ \text{g} = 15\ \text{g}$.

Now determine the weight of water: $250\ \text{g} - 15\ \text{g} = 235\ \text{g}$. It follows that 250 g of a 6 per cent solution of sodium chloride can be prepared by dissolving 15 g of the salt in 235 g of water. To do this, 15 g of sodium chloride are weighed out on a balance and 235 ml of distilled water are measured out by a calibrated vessel. Distilled water is placed in a beaker containing the salt and the mixture is stirred to complete dissolution.

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1. What is the weight fraction (concentration) of solute and how can it be expressed?
2. What quantity of sodium chloride (in grams) and water (in ml) are required to prepare (a) 120 g of a 5 per cent solution, (b) 25 g of a 0.5 per cent solution, and (c) 120 kg of an 8 per cent solution?
3. 15 g of salt are dissolved in 135 ml of water. What is the weight fraction of the salt in this solution?
4. When 50 g of potassium nitrate solution were evaporated the solid residue weighed 0.5 g. What was the weight fraction of the salt in the initial solution?
5. The weight of a 10 per cent solution of sulphuric acid is 500 g. Determine the weight fraction of sulphuric acid in the solution if it is diluted with water to produce 0.5 litre.

4.4 Solutions in Nature, Industry, Agriculture, and in the Home

Solutions play a very important role in nature. Many natural rocks were formed from solutions. Plants take the necessary nutrition from soil in the form of solutions. The timely supply of water is therefore a prerequisite condition for obtaining abundant harvests. Mineral fertilizers are often used as solutions in agriculture. Pests and weeds are also controlled by applying special solutions.

Assimilation of foods by man and animals is also achieved through their congestion in the alimentary tract where food is converted into substances soluble in water.

In our studies we often use solutions instead of pure substances. Preliminary dissolution of reactants accelerates reactions between them. Huge amounts of water are used in the chemical industry for preparing solutions. Other industries also consume immense quantities of water.

Pure substances are obtained by their dissolution, filtration (by which impurities are separated) and subsequent crystallization. Benzine, alcohol, and other liquids are also used for the dissolution of substances. Fat may be removed from our clothes by benzine. Fats are insoluble in water, but when acted upon by benzine they are easily dissolved and removed from fabric in the form of solution. Organic solvents are widely used for extraction of oils from various seeds of plants.

4.5 Composition of Water

We have already proved that water consists of hydrogen and oxygen when we burned hydrogen in oxygen. We also know that decomposition of water by electrolysis gives hydrogen and oxygen. Hydrogen combines with oxygen to form water in the same proportions (2 : 1) in which these gases are liberated during decomposition of water. This can be confirmed by carrying out an experiment in an apparatus known as an eudiometer (Fig. 4.6). The apparatus consists of a thick-walled tube sealed tightly at one end with a rubber stopper through which copper wires are passed. The tube is marked by equally spaced divisions on the outer side of the tube. An eudiometer is filled with water, overturned, and its open end is placed in a beaker containing water so that water should not flow out from the tube. Now oxygen is passed into the tube to lower the water level to the second mark (two volumes) while the next two volumes are filled with hydrogen. The wires of the eudiometer are now connected to the induction coil which in turn is connected to the source of electricity. As current passes in the circuit a spark is discharged in the eudiometer to explode the hydrogen-oxygen mixture. The water level rises exactly three divisions. If we want to know which gas remains in the eudiometer after the explosion, the open end of the tube is covered with a stopper, the eudiometer is removed from the stand, and overturned. The stopper is now removed and a glowing splint is put to the mouth of the tube: the splint catches fire. This indicates that the

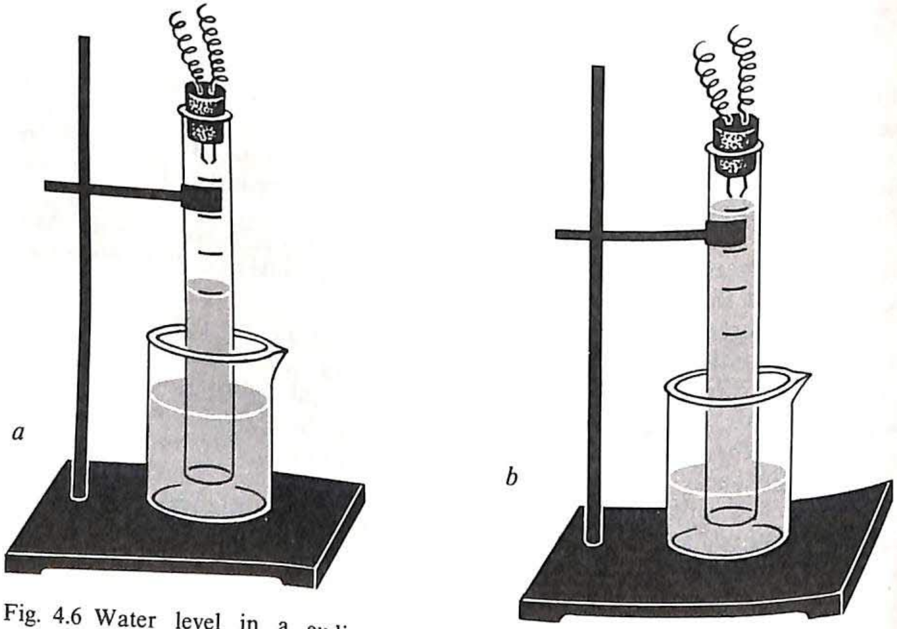

Fig. 4.6 Water level in a eudiometer: *a* – before explosion; *b* – after explosion

remaining gas is oxygen (one volume). This also indicates that oxygen and hydrogen were consumed in the reaction (explosion) in the ratio of 1 : 2.

Our knowledge that two volumes of hydrogen are evolved per one volume of oxygen during decomposition of water, and that the same gases are consumed in the same proportions during formation of water, allows us to calculate the weight fractions (concentration) of hydrogen and oxygen in water and the weight ratio of the elements in water. Let us assume that 1 litre of oxygen has been evolved during decomposition of water; this means that two litres of hydrogen have been evolved during this process. Once we know that the weight of one litre of hydrogen is 0.089 g, while one litre of oxygen weighs 1.429 g we can calculate the weight ratio of hydrogen and oxygen in water:

$$0.178\ \text{g} : 1.429\ \text{g} = 1 : 8$$

which means that eight parts by weight of oxygen are present per one part by weight of hydrogen in water. From this ratio one can determine weight fractions of the elements in water once we know that water weight is composed of 9 weight fractions (1 weight fraction + 8 weight fractions):

$1 : 9 = 0.11$ or 11 per cent of hydrogen

$8 : 9 = 0.89$ per 89 per cent of oxygen

?
△

1. By what two methods can it be proved that water consists of hydrogen and oxygen?
2. Describe the experiment in which water is decomposed by electric current.
3. Describe the experiment in which water is formed in an eudiometer.
4. An eudiometer contains a mixture of hydrogen with oxygen, both gases being taken in the quantity of 12 ml. Which gas remains in the eudiometer after an explosion, and in what quantity?
5. Hydrogen peroxide contains 16 parts by weight of oxygen per one part by weight of hydrogen. Since we know the atomic weights of hydrogen and oxygen and the molecular weight of hydrogen peroxide (34), derive the chemical formula of this substance.
6. During decomposition of water by electric current, 100 ml of hydrogen were formed. Determine the amount of oxygen that was formed during this reaction.

4.6 Chemical Properties of Water

Hydrogen is combustible and oxygen supports burning, whereas water is neither combustible nor does it support burning of common combustible substances. On the contrary, water quenches fire. Why does hydrogen lose its combustibility after it has combined with oxygen, and why does oxygen lose its ability to support burning?

The burning of hydrogen is the reaction of combination of hydrogen with oxygen. With what substances does water react?

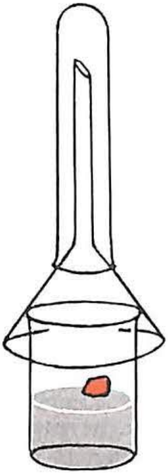

Fig. 4.7 Reaction of sodium with water

Reaction of Water with Metals. Fill a glass cylinder with water and into it drop calcium shavings: gas bubbles begin separating from the calcium's surface (as with zinc placed in sulphuric acid solution). If a burning splint is put to the mouth of the cylinder, we shall observe flashes. This is hydrogen burning. Water in the cylinder becomes cloudy. The white suspended particles are calcium hydroxide $Ca(OH)_2$. The reaction can be described as follows

$$Ca + H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$$

During this reaction, which occurs at room temperature, one atom of hydrogen is displaced from the water molecule (H—OH), while the other atom remains connected with the oxygen atom, and passes as the OH group into the composition of calcium hydroxide. Since the atom of calcium is divalent, it displaces two hydrogen atoms from two water molecules, while the remaining two OH groups combine with the calcium atom:

$$Ca + 2HOH = Ca(OH)_2 + H_2\uparrow$$

The reaction is even more energetic with sodium. Drop a small piece of sodium into a beaker containing water. Sodium will float to the surface of the water, upon which it melts to form a lustrous drop. The drop moves rapidly about on the water surface with a hissing sound and gradually diminishes in size until it disappears completely. If we now evaporate the solution, a white substance will remain. This is sodium hydroxide NaOH. If the reaction of sodium with water is carried out in the apparatus shown in Fig. 4.7, the test tube will be filled with hydrogen which is easy to identify. It follows that the reaction of water with sodium gives sodium hydroxide and hydrogen:

$$2Na + 2HOH = 2NaOH + H_2\uparrow$$

Sodium and calcium belong to the group of most active metals (see the electrochemical series).

Fig. 4.8 Preparing calcium hydroxide

In considering the reactions of water with metals we have established a very important property of water: it reacts with active metals (potassium, sodium, calcium, barium, and some others) to release half its own hydrogen and to form compounds with the composition of Me(OH)$_n$ (where Me is the metal and n is the number equal to the valency of the metal).

Now let us see if water can react with oxides.

Reaction of Water with Oxides of Nonmetals. Put a small quantity of water into a beaker, burn red phosphorus in a spoon in the beaker, and then wait until the phosphorus(V) oxide so formed (P_2O_5) is dissolved. Now add a few drops of litmus: the violet colour of litmus changes to red to indicate that the solution contains acid. Phosphorus(V) oxide combines with water to give phosphoric acid H_3PO_4:

$$P_2O_5 + 3H_2O = 2H_3PO_4$$

Now pour a small quantity of water into a beaker and burn sulphur as in the previous experiment. Try this solution with litmus: it also turns red. The oxide of sulphur (IV) SO_2 that was formed during the burning of sulphur has combined with water to form sulphurous acid H_2SO_3

$$SO_2 + H_2O = H_2SO_3$$

Sulphur may display different valencies in its reactions. Apart from the oxide SO_2, in which sulphur is tetravalent, it may form the oxide SO_3, in which sulphur is hexavalent (VI). Sulphur(VI) oxide reacts with water to form the acid which we already know, viz. sulphuric acid H_2SO_4

$$SO_3 + H_2O = H_2SO_4$$

Nitrogen forms the oxide N_2O_5 which combines with water to give nitric acid, which is also known to us

$$N_2O_5 + H_2O = 2HNO_3$$

Compounds of oxides of nonmetals with water are acids.

Reaction of Water with Metal Oxides. Consider now the reaction of water with metal oxides. Place small quantities of copper(II) oxide CuO, iron(III) oxide Fe_2O_3, zinc oxide ZnO, and calcium oxide CaO in separate beakers and add small quantities of water to each beaker. Copper oxide, iron oxide and zinc oxide are not dissolved in water, nor do they combine with it in any other way; calcium oxide, however, (which is known as burnt lime or quicklime) behaves differently.

When water is poured over quicklime much heat is liberated and part of the water evaporates, while lumps of quicklime break into pieces and turn into a loose powder, known as slaked lime, or calcium hydroxide $Ca(OH)_2$ (see Fig. 4.8):

$$CaO + H_2O = Ca(OH)_2$$

Oxides of sodium and potassium react with water in a similar way:

$$Na_2O + H_2O = 2NaOH$$
$$K_2O + H_2O = 2KOH$$

These reactions give sodium hydroxide NaOH and potassium hydroxide KOH.

To summarize, some metal oxides (the majority of them) do not react with water while others react to give hydroxides. Metal oxide combines with water to form *bases*.

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△

1. Describe the chemical properties of water.
2. If water vapour is passed through a hot iron tube hydrogen is liberated and iron oxide (Fe_3O_4) is formed on the interior surfaces of the tube. Write down the equation for this reaction. What type of reaction is it?
3. If phosphorus(V) oxide is stored in an open bottle its weight increases, whereas the weight of copper(II) oxide stored in an open bottle does not change with time. Explain.
4. What are the two methods by which calcium hydroxide may be formed? Write equations for the reactions.
5. When barium and barium oxide react with water, barium hydroxide is formed. Write down equations for the reactions. What type of reactions are they?
6. Name four metal oxides that react with water.
7. Name four metals that react with water.

4.7

Bases. Alkalis

Let us become acquainted with some metal hydroxides.

Sodium hydroxide NaOH is a white solid deliquescent in air, and readily soluble in water. When sodium hydroxide is dissolved in water, heat is liberated. Solutions of sodium hydroxide in water are soapy to the touch and very caustic. They destroy the skin, textiles, paper, and other materials – hence the name caustic soda. Sodium hydroxide and its solutions should be handled with special precautions so that they do not get onto the skin of the hands or face or clothes, footwear, etc. Sodium hydroxide causes heavy burns on the skin which do not heal for a long time. Sodium hydroxide and potassium hydroxide are called *lyes*.

If litmus is added to a solution of sodium hydroxide the colour of the litmus changes to blue. If a colourless alcoholic solution of phenolphthalein is added instead of litmus, the solution turns crimson; and methyl orange solution becomes yellow in solution of sodium hydroxide.

Potassium hydroxide KOH is also a white solid, readily soluble in water. Much heat is liberated during its dissolution in water. Like sodium hydroxide solution, the solution of potassium hydroxide is soapy to the touch and very caustic. The violet colour of litmus changes to blue in a solution of potassium hydroxide; a colourless solution of phenolphthalein becomes crimson; and the orange colour of methyl orange changes to yellow. Potassium hydroxide is thus similar to sodium hydroxide in some of its properties.

Calcium hydroxide $Ca(OH)_2$, known as slaked lime, is a loose white powder, slightly soluble in water. An aqueous solution of calcium hydroxide is called lime water. Lime water alters the colour of litmus from violet to blue, a colourless phenolphthalein solution becomes crimson, and methyl orange turns yellow.

Slaked lime is used in the manufacture of the mortar for masonry and wall plasters.

Sodium hydroxide, potassium hydroxide and calcium hydroxide are water-soluble bases.

Bases soluble in water are called alkalis.

Litmus, phenolphthalein, and methyl orange are indicators of acids and alkalis. Colours of the indicators in solutions of acids and alkalis are given in Table 4.1.

Table 4.1

Indicators

Indicator	Colour in various solutions		
	neutral	acid	alkaline
Litmus	violet	red	blue
Methyl orange	orange	pink	yellow
Phenolphthalein	(none)	(none)	crimson

In addition to the few water-soluble bases there are a great many insoluble ones, such as copper(II) hydroxide $Cu(OH)_2$, ferric hydroxide $Fe(OH)_3$, etc. Their composition is like that of water-soluble bases but they cannot be obtained by combining the metal oxide with water. When heated, they decompose to give the oxide and water:

$$Cu(OH)_2 = CuO + H_2O \qquad 2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

Bases can thus be classified as soluble (alkalis) or insoluble in water. All bases have a similar composition: they comprise a metal and the OH group (known as the *hydroxyl group*). The latter can be regarded as a residue of the water molecule from which one hydrogen atom has been subtracted: H—OH.

The hydroxyl group is connected in the water molecule with one hydrogen atom and is therefore univalent. And since the hydroxyl group is univalent, one metal atom can combine with that number of hydroxyl groups which is equal to the valency of the metal. Univalent atoms of sodium and potassium can combine with one hydroxyl group, divalent atoms of calcium and copper with two, tervalent atoms of iron with three hydroxyl groups, etc. Once we know the valency of metals we can derive formulas for metal hydroxides by adding hydroxyl groups in the quantity determined by the valency of the metal. The formula of barium hydroxide, for example, is $\overset{II}{Ba}(OH)_2$.

A base is a compound in which each atom of metal is combined with one or several hydroxyl groups.

1. Describe properties of (a) sodium hydroxide, (b) calcium hydroxide.
2. How are bases classified? Give examples of bases belonging to the main two groups.
3. How do alkalis change the colour of (a) litmus, (b) phenolphtalein, (c) methyl orange?
4. Write formulas of (a) aluminium hydroxide, (b) magnesium hydroxide, (c) chromium(III) hydroxide.
5. Write out separately the formulas of (a) oxides, (b) bases, (c) acids, and (d) salts included in the following: CaO, H_2SO_4, $Fe(OH)_2$, $FeSO_4$, $CaSO_4$, HCl, LiOH, MnO, $CuCl_2$, $Mn(OH)_2$, SO_2.
6. Make out formulas for the oxides corresponding to the following bases: KOH, $Cu(OH)_2$, $Fe(OH)_3$, $Cr(OH)_2$. Name them.
7. Make out formulas for the bases corresponding to the following oxides: CuO, FeO, Li_2O, BaO. Name them.

4.8

Neutralization Reaction

We have studied reactions of acids with metals and metal oxides. These reactions give salts of corresponding metals. Bases also contain metals and one can suggest that acids react with bases to give salts as well.

Add hydrochloric acid HCl to a solution of sodium hydroxide NaOH: the solution remains clear and colourless but if we touch the test tube we can easily note that it has become warm which indicates that a chemical reaction has taken place between the acid and alkali.

In order to establish the character of this reaction, let us carry out the following experiment. Dip a litmus paper into the alkali solution. Of course it turns blue. Now add, in small portions, acid from a burette (Fig. 4.9) until the litmus colour changes to violet. If the initial violet colour is restored, this indicates that the solution does not now contain an alkali. But the violet

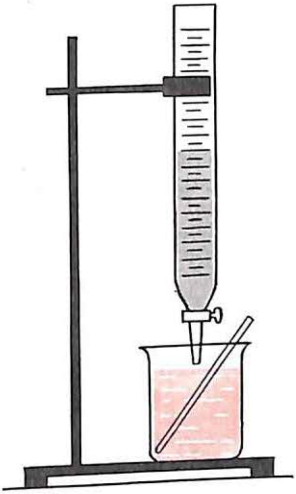

Fig. 4.9 Neutralization reaction

colour of the indicator shows also that the mixture does not contain acid either, because the colour of litmus in acid is red. The solution is neutral. Evaporate the solution: the white precipitate is table salt NaCl.

The reaction between sodium hydroxide and hydrochloric acid can be expressed as follows:

$$NaOH + HCl = NaCl + H_2O$$

The essence of this reaction is that the sodium atoms and the atoms of hydrogen change places. As a result, the hydrogen atom of the acid combines with the hydroxyl group of the alkali to give a molecule of water, while the metal atom combines with the acid radical (residue) Cl to form the salt. This reaction can be referred to the class of exchange reactions.

Do insoluble bases react with acids? Place blue copper(II) hydroxide $Cu(OH)_2$ in a beaker and add water: cupric hydroxide does not dissolve. Now place cupric hydroxide into another beaker and add nitric acid: the solid dissolves to give a clear blue solution of copper(II) nitrate. The equation of the reaction is:

$$Cu(OH)_2 + 2HNO_3 = Cu(NO_3)_2 + 2H_2O$$

Like alkalis, insoluble bases react with acids to give salts and water.

A reaction between an acid and a base that gives a salt and water is called a neutralization reaction.

The name neutralization is given to the reaction because the initial substances that have acid and alkaline properties, give a product which is devoid of either of them (neither acid nor alkaline). The reaction product is neutral.

The neutralization reaction is used to test experimentally the properties of insoluble hydroxides. If they react with alkalis they are referred to acids and the formula of such a hydroxide should then be written as the formula of an acid. If the hydroxide enters the neutralization reaction with an acid, it should be referred to a base and its formula should be written as that of alkalis: $Me(OH)_n$ by which we emphasize the presence of the hydroxyl group in it. The name hydroxide will normally be attributed to bases.

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1. What reactions are called reactions of neutralization?
2. Write equations for reactions between (a) hydrochloric acid and magnesium hydroxide, (b) nitric acid and iron(III) hydroxide, (c) sulphuric acid and potassium hydroxide, (d) phosphoric acid and calcium hydroxide.
3. What are the differences between chemical properties of bases and acids?
4. Write the equation for a neutralization reaction between sodium hydroxide and sulphuric acid and determine in what proportions (by weight) these substances react with each other.
5. Which of the following substances will react with hydrochloric acid: zinc, iron(III) oxide, barium hydroxide, mercury? Write equations of the corresponding reactions.

4.9 Reactions of Alkalis with Nonmetal Oxides

We already know that some oxides react with acids to form salts and water. But some other oxides (of carbon(IV), sulphur(IV) or phosphorus(V)) do not react with acids to give salts and water. So let us test their reaction with alkalis.

Fill a dry flask with carbon dioxide gas and drop a grain of sodium hydroxide into it. Stopper the flask with a rubber plug through which a glass tube is passed: a rubber tube is attached to it and has a clamp fastened on it as shown in Fig. 4.10. Touch the flask with your hand: it feels warm. Droplets of water can be seen forming on the inner walls of the flask. All these are signs that a chemical reaction is occurring inside the flask. If carbon dioxide reacts with sodium hydroxide, one can suggest that a certain rarefaction (vacuum) has been created inside the flask. Allow the flask to cool to 20–25 °C, lower the end of the rubber tube into a dish filled with water and release the clamp on the rubber tube: water will be sucked into the flask which indicates that our conjecture was correct and that carbon dioxide has reacted with sodium hydroxide. One of the reaction products is water. What is the composition of the solid reaction product?

The oxide of carbon(IV) is known to give carbonic acid H_2CO_3. The solid substance formed in the flask is the salt of carbonic acid, sodium carbonate Na_2CO_3.

Two molecules of sodium hydroxide are required to form one molecule of sodium carbonate:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

Carbon dioxide reacts with sodium hydroxide to give the salt sodium carbonate Na_2CO_3 and water.

There are many other oxides (SO_2, SO_3, SiO_2, P_2O_5, etc.) that react with alkalis to form salts and water.

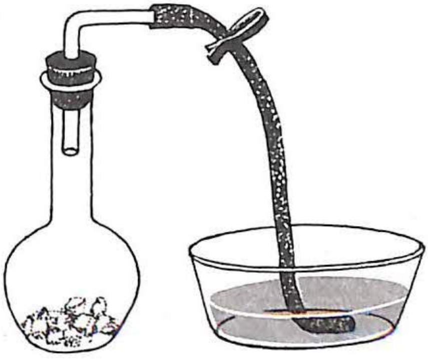

Fig. 4.10 Reaction of sodium hydroxide with carbon dioxide

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1. As air was passed through a barium hydroxide solution it became cloudy. What gas is responsible for cloudiness in the solution? What substance is precipitated? Write the reaction equation.

△

2. Of the following substances: carbon (IV) oxide, phosphorus (V) oxide, copper (II) oxide, sulphur (VI) oxide, and barium oxide, which will react with: (a) water, (b) hydrochloric acid, (c) potassium hydroxide solution? Write down equations for the reactions that may occur and name all substances.

3. Place sulphur (IV) oxide in a flask and add potassium hydroxide solution. Stopper the flask immediately and shake it. Will the atmosphere in the flask rarefy?
Give reasons for your answer.

4.10 Classification of Oxides

The known chemical properties of oxides can be used for their classification.

Oxides that react with acids to form a salt and water are known as basic.

The name is given to these oxides because each basic oxide gives a base:

$$CuO—Cu(OH)_2; \quad MgO—Mg(OH)_2; \quad Fe_2O_3—Fe(OH)_3$$

Basic oxides are formed by metals only, e. g. MgO (magnesium oxide), CaO (calcium oxide), BaO (barium oxide), etc.

Oxides that react with bases to form a salt and water are called acidic.

This name is given to them because each acid oxide gives the corresponding acid:

$$CO_2—H_2CO_3; \ SO_2—H_2SO_3; \ SiO_2—H_2SiO_3; \ P_2O_5—H_3PO_4$$

Acid oxides are formed by nonmetals and some metals: sulphur (IV) oxide SO_2, sulphur (VI) oxide SO_3, phosphorus (V) oxide P_2O_5, chromium (VI) oxide CrO_3, manganese (VII) oxide Mn_2O_7.

Some metals form both basic and acid oxides. These are, for example, chromium and manganese. Their valency is variable. The oxides in which chromium and manganese exhibit their lower (II) valency are basic oxides: chromous oxide CrO and manganous oxide MnO. Their corresponding bases are chromous hydroxide $Cr(OH)_2$, and manganous hydroxide $Mn(OH)_2$. The oxides, in which chromium and manganese are in their higher valencies are acid oxides: chromic (VI) oxide CrO_3 and manganic (VII) oxide Mn_2O_7. Their corresponding acids are chromic acid H_2CrO_4 and manganic acid $HMnO_4$.

?

1. Compare the properties of basic and acid oxides. Use the form of Table 4.2 below. What are the differences in chemical properties between bases and acids?

Table 4.2

Properties	Oxides	
	basic	acid
1. Reaction to water		
2. Reaction to acids		
3. Reaction to bases		

Δ

2. Given are substances whose composition is expressed by the following formulas: Na_2O, CO_2, CuO, SO_3, Fe_2O_3, BaO. Which of them will react with (a) hydrochloric acid, (b) sodium hydroxide? Write the corresponding reaction equations.

3. Write in separate columns the formulas of basic and acid oxides derived from the following: N_2O_5, BaO, P_2O_5, CaO, SO_3, NiO.

4. How can a basic oxide be distinguished experimentally from an acid one if both are soluble in water? Give examples in your answer. Write the reaction equations.

5. How can a basic oxide be distinguished experimentally from an acid one if both are insoluble in water? Give examples in your answer. Write the reaction equations.

6. Write the formulas of the oxides corresponding to the following hydroxides: $Cr(OH)_2$, $Cr(OH)_3$, $Al(OH)_3$, $Mn(OH)_2$.

7. What are the similar and different chemical properties of the following oxides: (a) CO_2 and SiO_2; (b) CuO and SiO_2; (c) BaO and CO_2? Give the corresponding reaction equations to prove your answers.

8. Write equations for the reactions by which the following conversions may be achieved:

a)
$$\begin{tikzcd} & KOH \\ K_2O \arrow[ur] \arrow[dr] & \\ & KCl \end{tikzcd}$$

(b) $P \rightarrow P_2O_5 \rightarrow H_3PO_4$

c)
$$\begin{tikzcd} & & Ba(OH)_2 \\ Ba \arrow[r] & BaO \arrow[ur] \arrow[dr] & \\ & & Ba(NO_3)_2 \end{tikzcd}$$

(d)
$$\begin{tikzcd} & & H_2CO_3 \\ C \arrow[r] & CO_2 \arrow[ur] \arrow[dr] & \\ & & CaCO_3 \end{tikzcd}$$

5

Main Classes of Inorganic Compounds

5.1 Composition and Names of Oxides, Bases, Acids, and Salts

We have studied two chemical elements, viz. oxygen and hydrogen, and their most important chemical compounds and have acquainted ourselves with the main classes of chemical compounds – oxides, bases, acids, and salts. We have paid special attention to their general chemical properties and this will make the study of new chemical elements easier because the chemical properties of elements are mainly characterized by the composition and properties of their oxides and hydroxides.

Let us try to systematize our knowledge. First of all try to remember what is the difference in composition of compounds in each class. To do this, perform the following exercises.

?

1. Write out the formulas of: (a) oxides, (b) bases, (c) acids, and (d) salts from the following: $Ca(OH)_2$, Na_2O, HNO_3, $Cu(OH)_2$, $FeCl_3$, $CaSO_4$, Cr_2O_3, HCl, K_2O, H_3PO_4, $Fe(OH)_3$, $CuCl_2$, Na_2SO_4, H_2SO_4, $Ba(OH)_2$, PbO, CaO, H_2SO_3, $Al_2(SO_4)_3$, H_2S, $AgNO_3$, FeS, $Ca(NO_3)_2$. Name each substance.

△

2. Make out the formulas and name the oxides and hydroxides of the following elements: potassium, zinc, aluminium, sodium, magnesium, iron (III).

3. What substances are known as alkalis? Give formulas of three alkalis and name them.

4. Write the formulas and names of salts formed by aluminium with the following acids: hydrochloric, nitric, sulphuric, phosphoric, carbonic, silicic, manganic.

5. Compare the composition of: (a) acids and salts, (b) bases and salts. How do they differ and what do they have in common?

6. What substances are known as oxides, acids, bases, and salts?

7. Into what two main groups are all oxides divided according to their chemical properties?

Oxides

In order to characterize general properties of oxides, try to remember what substances are called oxides, and give examples (see Secs. 2.3 and 4.10).

We now know two groups of oxides, namely acid and basic oxides, and have studied their chemical properties. Let us systematize our knowledge of oxides.

5.2 Chemical Properties of Oxides

Reaction of Basic Oxides with Water. Some basic oxides, for example those formed by the metals–sodium, potassium, barium and calcium–react with water to form bases (alkalis), for example:

$$CaO + H_2O = Ca(OH)_2$$

calcium
hydroxide

Many basic oxides, e.g. copper(II) oxide or iron(II) oxide, do not react with water but they still have the corresponding bases.

Reaction of Basic Oxides with Acids. All basic oxides react with acids to form salts and water, for example

$$MgO + H_2SO_4 = MgSO_4 + H_2O$$

magnesium
sulphate

Reaction of Acid Oxides with Water. Acid oxides react with water to form acids, for example

$$SO_3 + H_2O = H_2SO_4$$

sulphuric
acid

Some acid oxides, e.g. the oxide of silicon(IV) SiO_2, do not react with water but they still have corresponding acids.

Reaction of Acid Oxides with Bases. All acid oxides react with alkalis to form a salt and water, for example,

$$Ba(OH)_2 + C_2O = BaCO_3 + H_2O$$

barium
carbonate

?

△ 1. Write equations for the reactions with water of the following oxides: sodium oxide, sulphur(IV) oxide, barium oxide, phosphorus(V) oxide. Name the reaction products.

2. Write equations for the following reactions: (a) calcium oxide with nitric acid, (b) ferric oxide with sulphuric acid, (c) magnesium oxide with hydrochloric acid. Name the reaction products.

3. Write equations for the reactions between (a) sulphur(IV) oxide and potassium hydroxide, (b) carbon(IV) oxide and barium hydroxide, (c) silicon(IV) oxide and sodium hydroxide. Name the reaction products.

4. Write formulas of oxides corresponding to the following hydroxides: KOH, $Ba(OH)_2$, H_3PO_4, H_2SiO_3, $Fe(OH)_2$, H_2SO_3, $Cr(OH)_2$. Indicate which of them are basic and which are acid oxides.

5. Which of the following oxides Na_2O, SO_3, MgO, CO_2, MnO may react with (a) nitric acid and (b) potassium hydroxide? Write down the reaction equations and name the reaction products.

6. Write down equations for the reactions by which the following conversions may be achieved:

$$\text{(a) } Na_2O \begin{matrix} \nearrow NaOH \\ \searrow NaNO_3 \end{matrix} \qquad \text{(b) } C \rightarrow CO_2 \begin{matrix} \nearrow H_2CO_3 \\ \searrow K_2CO_3 \end{matrix}$$

Acids

In order to summarize the properties of acids, remember what compounds are known as acids, and give examples (see Secs. 3.4-3.6).

5.3 Classification of Acids

By their composition all acids are classified as *binary* and *oxyacids*. The former contain only hydrogen and a nonmetal, e.g. hydrofluoric acid HF, hydrochloric acid HCl, hydrobromic acid HBr, hydriodic acid HI, hydrosulphuric acid H_2S; the oxyacids contain oxygen, hydrogen, and a nonmetal, e.g. sulphurous acid H_2SO_3, sulphuric acid H_2SO_4, nitric acid HNO_3, phosphoric acid H_3PO_4, carbonic acid H_2CO_3, silicic acid H_2SiO_3.

By the number of hydrogen atoms in a molecule of an acid that are capable of being substituted for by metals, acids are also classified as monobasic (HCl, HNO_3), dibasic (H_2SO_4, H_2CO_3, H_2S, H_2SO_3), and tribasic (H_3PO_4).

△

Below follow the formulas of acid residues in which their valency is designated by the corresponding number of dashes $\equiv AsO_4$, $-ClO_4$, $=CrO_4$, $=S$, $-F$, $-MnO_4$, $-VO_3$, $\equiv PO_4$, $=SeO_4$. Write the formulas of the corresponding acids and divide them into the following groups: (a) oxyacids, (b) binary acids, (c) monobasic acids, (d) dibasic, and (e) tribasic acids.

5.4 Chemical Properties of Acids

What we know about acids is enough to characterize their chemical properties.

Action of Acids on Indicators. Most acids readily dissolve in water. Of all the acids you have met so far silicic acid alone is practically insoluble in water.

Acid solutions change the colour of indicators: litmus and methyl orange both turn red. This reaction is used for identification of acids among other compounds.

Reaction of Acids with Bases. Acids react with bases to form a salt and water:

$$\mathrm{HCl + NaOH = \underset{\substack{\text{sodium}\\\text{chloride}}}{NaCl} + H_2O}$$

$$\mathrm{3H_2SO_4 + 2Fe(OH)_3 = \underset{\substack{\text{ferric}\\\text{sulphate}}}{Fe_2(SO_4)_3} + 6H_2O}$$

The reaction of acids with bases is already known to us. It is called a neutralization reaction.

Reaction of Acids with Basic Oxides. Acids react with basic oxides to form a salt and water:

$$\mathrm{2HCl + CuO = \underset{\substack{\text{cupric}\\\text{chloride}}}{CuCl_2} + H_2O}$$

$$\mathrm{H_2SO_4 + MgO = \underset{\substack{\text{magnesium}\\\text{sulphate}}}{MgSO_4} + H_2O}$$

Reactions with basic oxides are used in the manufacture of some salts and also for the purification of metals (that are themselves insoluble in acid) from their oxides.

Reaction of Acids with Metals. Solutions of some acids (sulphuric, hydrochloric, phosphoric, etc.) react with metals that come before hydrogen in the electrochemical series (p. 70). The reaction gives a salt and hydrogen:

$$\mathrm{2HCl + Zn = \underset{\substack{\text{zinc}\\\text{chloride}}}{ZnCl_2} + H_2\uparrow}$$

$$\mathrm{H_2SO_4 + Fe = \underset{\substack{\text{ferrous}\\\text{sulphate}}}{FeSO_4} + H_2\uparrow}$$

Nitric acid reacts with metals to give salts but without liberation of hydrogen.

The properties characteristic of acids are not inherent in all representatives of the compounds belonging to the class of acids. For example, acids that are insoluble in water do not react with metals; nor can they be identified by indicators.

? 1. Describe the chemical properties of acids. Use indicators to illustrate your answer.

△ 2. What is a neutralization reaction? What are the products of a neutralization reaction?

3. How can a solution of sulphuric acid be neutralized practically with potassium hydroxide solution? Write the reaction equation.

Reaction of Acids with Bases. Acids react with bases to form a salt and water:

$$HCl + NaOH = \underset{\text{sodium chloride}}{NaCl} + H_2O$$

$$3H_2SO_4 + 2Fe(OH)_3 = \underset{\text{ferric sulphate}}{Fe_2(SO_4)_3} + 6H_2O$$

The reaction of acids with bases is already known to us. It is called a neutralization reaction.

Reaction of Acids with Basic Oxides. Acids react with basic oxides to form a salt and water:

$$2HCl + CuO = \underset{\text{cupric chloride}}{CuCl_2} + H_2O$$

$$H_2SO_4 + MgO = \underset{\text{magnesium sulphate}}{MgSO_4} + H_2O$$

Reactions with basic oxides are used in the manufacture of some salts and also for the purification of metals (that are themselves insoluble in acid) from their oxides.

Reaction of Acids with Metals. Solutions of some acids (sulphuric, hydrochloric, phosphoric, etc.) react with metals that come before hydrogen in the electrochemical series (p. 70). The reaction gives a salt and hydrogen:

$$2HCl + Zn = \underset{\text{zinc chloride}}{ZnCl_2} + H_2\uparrow$$

$$H_2SO_4 + Fe = \underset{\text{ferrous sulphate}}{FeSO_4} + H_2\uparrow$$

Nitric acid reacts with metals to give salts but without liberation of hydrogen.

The properties characteristic of acids are not inherent in all representatives of the compounds belonging to the class of acids. For example, acids that are insoluble in water do not react with metals; nor can they be identified by indicators.

?

△

1. Describe the chemical properties of acids. Use indicators to illustrate your answer.
2. What is a neutralization reaction? What are the products of a neutralization reaction?
3. How can a solution of sulphuric acid be neutralized practically with potassium hydroxide solution? Write the reaction equation.

4. Write down equations for the reactions between (a) sulphuric acid and hydroxides of barium, aluminium, zinc, and potassium; (b) nitric acid and hydroxides of calcium, iron (III), lead (II) and sodium.
5. Write down the formulas of the following acids: HBr, H_2S, H_2SO_3, H_3PO_4, HNO_3, HI, H_2CO_3, H_2SO_4, H_2SiO_3, HF. Name the acids. Superscribe the Roman numerals to indicate the valency of acid residues in these acids.
6. Write the formulas and name the oxides corresponding to the following acids: H_2SO_3, H_2SO_4, H_2SiO_3, H_3PO_4.
7. Which of the following compounds can react with hydrochloric acid: Cu, CuO, $Cu(OH)_2$, Fe, Zn, ZnO, $Zn(OH)_2$, Ag? Write equations for the reactions that may occur and name the substances.
8. Into separate test tubes are placed Fe_2O_3, Mg, and solutions of NaOH, HCl, and phenolphthalein. What reactions characteristic of acids can be carried out with these reagents? Write the reaction equations.

Bases

Before reading further, remember what substances are known as bases and give examples (see Secs. 4.7-4.9).

5.5 Classification of Bases and Their Chemical Properties

All bases are divided into two major groups, namely, insoluble bases and bases soluble in water (alkalis).

Alkali solutions are soapy to the touch, they destroy skin and fabrics, and are therefore called caustic. Examples of alkalis are potassium hydroxide KOH, sodium hydroxide NaOH, calcium hydroxide $Ca(OH)_2$, barium hydroxide $Ba(OH)_2$, etc.

Action of Soluble Bases on Indicators. Solutions of bases change the colour of indicators: litmus turns blue, methyl orange yellow, and phenolphthalein crimson. This property of bases is used for their detection among other substances.

Reaction of Bases with Acids. All bases react with acids to form salt and water:

$$2HCl + Ca(OH)_2 = \underset{\substack{\text{calcium} \\ \text{chloride}}}{CaCl_2} + 2H_2O$$

$$2HCl + Cu(OH)_2 = \underset{\substack{\text{cupric} \\ \text{chloride}}}{CuCl_2} + 2H_2O$$

Reaction of Bases with Acid Oxides. Soluble bases react with acid oxides to give salts and water:

$$2NaOH + CO_2 = \underset{\substack{\text{sodium} \\ \text{carbonate}}}{Na_2CO_3} + H_2O$$

Decomposition of Bases by Heat. Insoluble bases easily decompose on heating to give the corresponding oxide and water:

$$Cu(OH)_2 = \underset{\text{cupric oxide}}{CuO} + H_2O$$

Alkalis decompose only at high temperatures.

?

△

1. Describe chemical properties of bases. Carry out the corresponding experiments.
2. Compare the chemical properties of alkalis and insoluble bases. Which of them are similar and which are different?
3. Write formulas for hydroxides of potassium, barium, magnesium, iron(III) and their corresponding oxides.
4. Which of the following substances will react with a sodium hydroxide solution, and which with hydrochloric acid: H_2SO_3, CuO, H_2S, $Mg(OH)_2$, SO_2, KOH, H_3PO_4, MgO, P_2O_5, $Cu(OH)_2$, CO_2, $Ca(OH)_2$? Write reaction equations.
5. Why should alkalis (KOH, NaOH) be kept from contact with the air (in tightly closed containers)? What changes may otherwise occur in alkalis? Write reaction equations.
6. How can the following chain of conversions be achieved: $Ca \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaCl_2$? Write reaction equations.
7. How can solution of acid and alkali contained in two separate test tubes be experimentally identified?

Salts

First read Sec. 3.5. Give examples of salts.

5.6

Naming of Salts and Their Composition

When we studied oxides, acids, and bases we dealt with the reactions by which salts are formed. Each salt may be regarded as a product of substitution of the hydrogen atoms of the acid by metal atoms.

Names of salts are formed from the name of the metal followed by the stem of the acid's name plus the appropriate suffix (see Sec. 3.5 and Table 3.2).

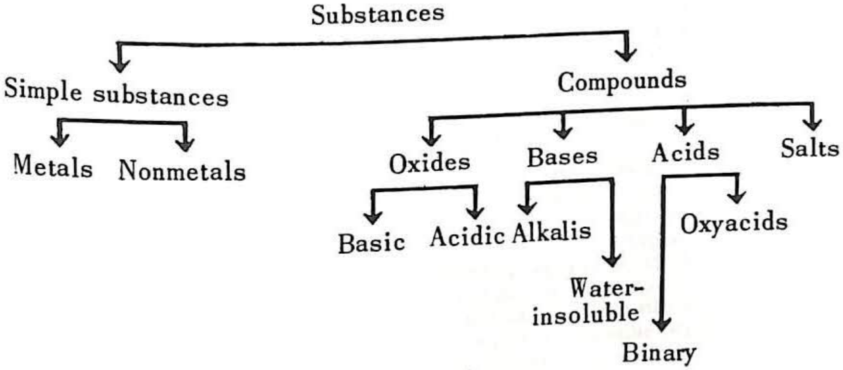
If a metal exhibits more than one valency, its valency is indicated by Roman numerals which follow the name of the metal in parentheses, e.g. $FeCl_3$ is iron(III) chloride while $FeCl_2$ is iron(II) chloride, $Fe_2(SO_4)_3$ is iron(III) sulphate, $FeSO_4$ is iron(II) sulphate, etc.

△

1. Rewrite the formulas of the salts and name them: $NaCl$, $BaSO_4$, $NaNO_3$, NaI, Na_2CO_3, Na_2S, Na_3PO_4, $CaBr_2$, NaF, Na_2SiO_3.
2. Write formulas for the following salts: aluminium sulphate, sodium sulphite, calcium nitrate, iron(III) bromide, magnesium phosphate, calcium fluoride, sodium bromide, potassium phosphate, magnesium nitrate, potassium silicate, sodium sulphate, copper(II) chloride.

5.7 Genetic Ties Between Oxides, Acids, and Salts

The substances that we have already studied can be divided into several classes according to their composition and properties. The ties between them can be represented by the following diagram:



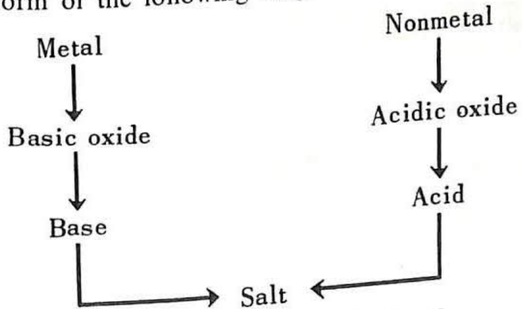
The study of oxides, bases, acids, and salts has shown that there exist certain connections between them: substances of one class can be obtained from substances of other classes. Two series of genetically connected substances can be distinguished. One begins with metals and the other with nonmetals. Barium is oxidized to barium oxide, and the latter reacts with water to give barium hydroxide, which in turn forms a salt when it reacts with acid. This chain of conversions can be shown as

$$Ba \rightarrow BaO \rightarrow Ba(OH)_2 \rightarrow BaCl_2$$

Phosphorus is oxidized to phosphorus(V) oxide, and the latter reacts with water to give phosphoric acid, which in turn reacts with alkali to form a salt. These conversions can be described as:

$$P \rightarrow P_2O_5 \rightarrow H_3PO_4 \rightarrow Na_3PO_4$$

These connections, based on the possibility of obtaining substances of one class from substances of other classes, are known as *genetic ties* (Latin *genus* means birth). The genetic ties between oxides, bases, acids, and salts can be shown in the form of the following diagram:



?

△

1. Describe oxides, bases and acids according to the following plan: (1) definition and composition; (2) chemical properties.
2. What substances are called salts? What is their composition?
3. How can the following chain of conversions be achieved:
(a) S → SO_2 → H_2SO_3 → K_2SO_3;
(b) Ca → CaO → $Ca(OH)_2$ → $Ca(NO_3)_2$?
Write reaction equations and indicate: (a) type of each reaction; (b) subscribe the class of each substance.
4. What do (a) acidic oxides and (b) basic oxides have in common, and in what do they differ?
5. Specify similarities and differences in composition of (a) acid and salt; (b) base and salt? Give examples.
6. Give examples to illustrate the genetic ties between different classes of substances as shown above. Write reaction equations.
7. Draw in your note-book the diagram showing the genetic ties between oxides, bases, acids and salts and interconnect (by two lines) those substances that can react with each other. Give corresponding reaction equations to illustrate the meaning of each line in your diagram.
8. How can the following conversions be realized:
(a) calcium → calcium oxide → calcium hydroxide → calcium nitrate;
(b) sulphur → sulphur(IV) oxide → sulphurous acid → calcium sulphite;
(c) copper(II) hydroxide → copper(II) oxide → copper(II) chloride;
(d) iron(III) hydroxide → iron(III) oxide → iron(III) sulphate?
Write equations for the corresponding reactions and name the reaction products.
9. Which of the following substances will react with one another: calcium oxide, calcium hydroxide, hydrochloric acid, sulphur(IV) oxide, zinc oxide, aluminium hydroxide, sodium hydroxide, magnesium hydroxide? Write equations for the reactions and specify the conditions under which these reactions can occur.
10. With substances of what classes can (a) bases, and (b) acids react? Write reaction equations.
11. With substances of what classes can (a) basic oxides and (b) acid oxides react? Write the corresponding reaction equations.

I. Laboratory Exercises

1. Properties of Substances

In studying chemistry one must be able to give a correct and complete description of substances. Describe the properties of a substance given to you by the instructor.

1. What is the normal physical state of this substance? What is its colour?

2. Smell the substance. Do not smell directly from the vessel because the vapour of the substance or gas can cause strong irritation of the airways. Instead act as follows: remove the stopper from the vessel and wave your hand over it towards the face as shown in Fig. I.1. The vapour will thus be strongly diluted with air and will not cause serious irritation.

If no smell can be detected at a distance, the vessel can be brought closer to the nose and smelled again.

3. Using a special scale, determine the relative hardness of the substance. If the scale is not available, try to scratch the solid with your finger-nail or a piece of glass. The hardness of the finger-nail is 2-2.5, and that of glass 5. If your nail leaves a line on the solid, its hardness can be assessed as below 2. If your nail does not leave any trace, try the reverse, i.e. scratch your nail with the test solid; if it marks the nail its hardness is above 2.5. Testing a substance with glass or standard scale specimens is done in the same way. This technique is used for approximate determination of the hardness of substances.

4. Test the substance for solubility. Take a small sample, put it in a test tube or a beaker, add water and shake. If the solid disappears or appreciably diminishes in size, the substance is said to be readily soluble.

Never close the mouth of the test tube with your finger when you shake the test tube because the solution may attack the skin or the solution itself may become contaminated. To shake the liquid, hold the test tube in your left hand as shown in Fig. I.2 and tap with the forefinger of the right hand on the lower part of the test tube. If the liquid in the test tube occupies more than half its volume, use a glass rod to stir it dipping the rod into the liquid several times; or the test tube may be stoppered and turned upside down several times as well.

5. Drop the test substance into a beaker or a test tube containing water. Does the solid sink or float to the surface? To obtain more accurate data on the density of the substance, consult a reference book.

6. Consult the reference book to determine the melting and boiling points of this substance.

7. From your own experience, make a judgement as to the plasticity, electrical conductivity, heat conductivity and some other properties of the test substance. If your experience is too limited, do not mention these properties.

8. In order to avoid accidental poisoning or irritation of the mouth mucosa, never taste an unknown substance. If the taste of the substance given for description is known to you, state it in your notes.

9. Describe the properties of the substance in the following order: physical state (aggregation), colour, odour, lustre, hardness, plasticity, electrical and heat conductivity, solubility in water, density, melting point and boiling point.

2. Separation of Mixtures

When deciding by what method shall the components of this or that mixture be separated, it is very important to know the properties of the individual components so that these may be conveniently used during their separation.

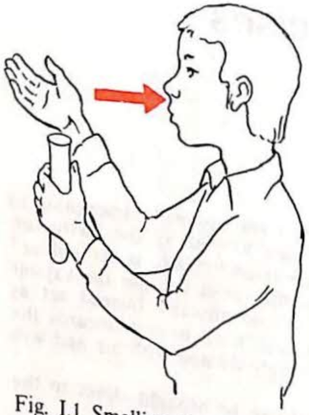


Fig. I.1 Smelling the odour of unknown substances

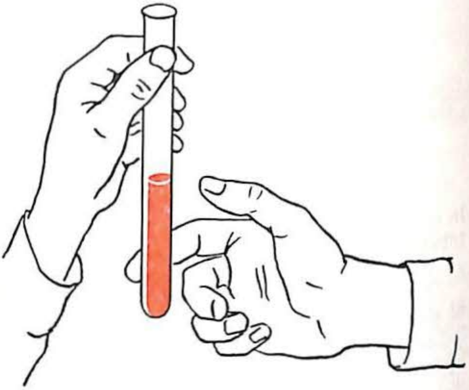


Fig. I.2 Stirring test-tube contents by tapping

1. Place a spoonful of powdered sulphur on a sheet of paper and the same amount of powdered iron (or iron filings) by alongside the first heap. Look attentively to memorize their colour.

2. Half fill two test tubes with water and drop a small amount of sulphur into one and of iron into the other test tube. Observe. (Remember that sulphur mixes poorly with water and therefore it floats to the surface, though its density is twice that of water.)

3. Apply a magnet to the sulphur on the sheet of paper and then to iron and observe.

4. Using a glass rod, mix the iron and sulphur thoroughly on the sheet of paper. What is the colour of the resultant mixture? Has the colour of the starting components (sulphur and iron) changed?

5. Place a pinch of the mixture into a test tube or a beaker containing water and observe. Compare your observations with those in point 2.

6. Cover the mixture on the paper with another sheet and put the magnet to the top of the paper. Lift the magnet. What has happened to the iron and sulphur?

Answer the following questions and draw a conclusion: do the initial components of the mixture (iron and sulphur) preserve their individual properties after they have been mixed? What difference in the physical properties of iron and sulphur has been used to separate them from their mixture?

3. Physical Phenomena

1. Take hold of one end of a glass tube and put it into the flame of a gas burner. Hold it horizontally. In a short while the tube will bend at the point where it was strongly heated. If an alcohol burner is used, the tube may be held at both ends (Fig. I.3). Then put its middle portion into the flame. When the glass becomes very hot, try to bend the tube. Has the glass been converted into some other substance by heating?

2. Put a piece of paraffin into a crucible, hold the latter with tongs or fix it in a metal ring stand. Put the crucible in the upper portion of the flame of the burner. What happens to the paraffin on heating? As soon as the paraffin has melted, place the crucible on a metal gauze sheet with an asbestos centre and put down the burner. When the crucible becomes cool, look at the paraffin. Has it turned into a new substance?

Is there anything common to the phenomena observed in the two experiments?

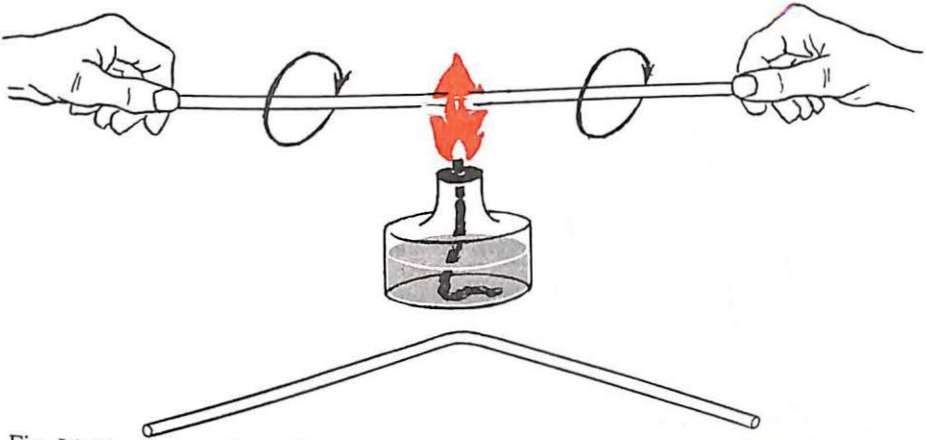


Fig. I.3 Bending a glass tube

4. Chemical Phenomena

1. Pick up a copper plate or wire with the test-tube holder (tongs) and hold it for a short while in the flame of a burner. Then remove the copper plate from the flame, and scrape off the black deposit on the copper's surface onto a sheet of paper using a knife or a splint. Heat the copper again and again scrape off the deposit. Has a new substance been formed during the heating of copper?

2. Place 3-5 pieces of marble or chalk (the size of a pea) in a small beaker. (Do it gently so as not to break the glass.) Add enough hydrochloric acid to cover the solid and observe. Light a match and put it into the beaker. What do you observe? Has a new substance been formed during the reaction of hydrochloric acid with marble (chalk)? What is the new substance?

What common phenomena have you observed in carrying out these two experiments?

5. Simple Substances and Compounds. Metals and Nonmetals

Look at the substances given to you by the instructor.

1. Read the label on the bottles containing the substances and divide them into two groups: simple substances and compounds. Arrange the bottles thus separated into two groups.

2. Look intently at all the simple substances and separate them into two other groups: metals and nonmetals. What property of metals have you used to identify them?

6. Decomposition of Copper Carbonate

1. Look at the powder of copper carbonate (malachite). What colour is it?

2. Place a small quantity of the powder into a test tube (the layer of the powder in the test tube should be 1-1.5 cm deep). Close the test tube with a stopper through which a glass (gas-outlet) tube is passed.

3. Test the assembled apparatus for tightness. To do so, lower the end of the gas-outlet tube into a beaker containing water to a depth of not over 0.5 cm and hold the test tube in your fist: air bubbles should be liberated into the water from the gas-outlet tube. Explain why. If air does not bubble from the gas-outlet tube it indicates that there is leakage between the stopper and the test tube or between the gas-outlet tube and the stopper. The stopper should be readjusted or replaced by a new one, and tightness of the apparatus tested again.

4. Lightly tap the test tube to distribute the malachite powder over the test-tube walls from the middle to the bottom of the test tube. Fix the test tube in the stand as shown in Fig. 1.13: its mouth should be slightly below the level of the bottom.

5. Put about 1 ml of lime water into a bottle or a beaker. Raise the apparatus in the stand and lower the gas-outlet tube into the lime water in the beaker.

6. First heat slightly the entire test tube and then heat the malachite powder beginning from the bottom and moving the burner in the direction of the test-tube mouth. Observe the changes that occur in the malachite and in the lime water.

7. When gas bubbles stop evolving, remove the end of the gas-outlet tube from the beaker containing lime water by raising the stand in a vertical direction. Put down the burner.

How has the colour of malachite changed on heating? What did you notice on the walls of the test tube near the stopper? What has happened to the lime water? What new substances have formed by heating the malachite? Why did we fix the test tube in the stand in an inclined position?

7. Reaction of Iron with Copper(II) Chloride Solution

1. Fill a test tube about 1/4 full of copper(II) chloride solution. Observe the colour of the solution.

2. Suspend an iron nail from a thread and lower it into the solution. Keep it in the solution for 1-2 minutes, then remove and examine it. What changes have occurred on the nail surface? Add a pinch of iron shavings to the same solution. Observe the change in colour of the solution. Compare it with the colour of iron(II) chloride $FeCl_2$ solution. What is the sign of the reaction that has occurred in the test tube? Write the equation of this reaction remembering that the formula of iron(II) chloride is $FeCl_2$ and of cupric chloride $CuCl_2$.

8. Acquaintance with Oxides

1. Look carefully at the samples of oxides given to you by the instructor and pay special attention to their physical state (aggregation), colour, and odour.

2. Draw the table given below in your note-book and fill in the data that you have gathered on the oxides:

Name of oxide	Composition (formula)	Physical properties		
		state of aggregation	colour	odour

9. Acquaintance with Fuels

1. Look carefully at samples of liquid and solid fuels given to you by the instructor.

2. Write in your note-book names of the fuels and briefly describe them.

10. Preparing Hydrogen

1. Hold a test tube in an inclined position, place 4-5 grains of zinc in it and add 2-3 ml of hydrochloric acid. Observe what happens on the surface of zinc and in the acid. What substance liberates?

Wait for a while until air is displaced from the test tube and put a burning match to the test-tube mouth. What will you observe?

2. When evolution of gas bubbles discontinues, transfer a few drops of the solution from the test tube onto a glass plate and evaporate the liquid over the burner (Fig. I.4). What remains on the glass after the liquid has evaporated? What are the products of the reaction between zinc and hydrochloric acid?

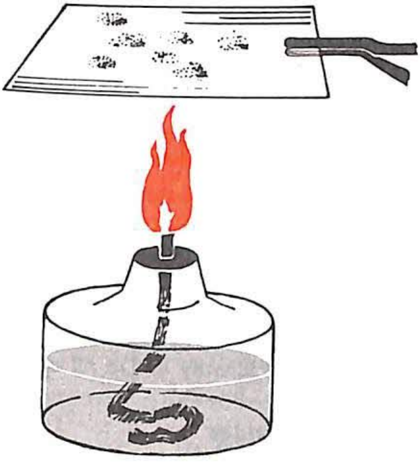


Fig. I.4 Evaporating solution on a glass plate

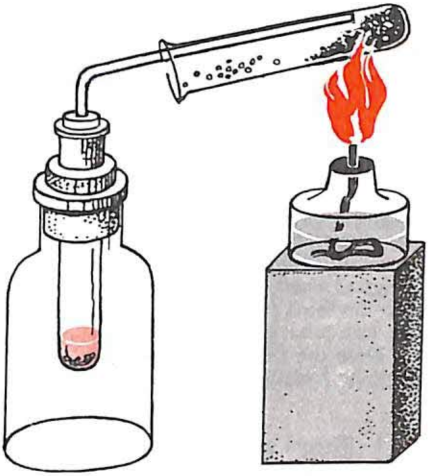


Fig. I.5 Apparatus for reduction of copper from its oxide by hydrogen

11. Reaction of Hydrogen with Copper(II) Oxide

1. Assemble an apparatus as shown in Fig. I.5, test it for tightness, place 8-10 grains of zinc in it, and add 4-5 ml of sulphuric acid. Close the test tube with a stopper through which a gas-outlet tube is passed. Fix the apparatus in a bottle or in a stand. Test the liberated hydrogen for purity and fit another test tube holding two grains of copper(II) oxide to the end of the gas-outlet tube so that its end should be over the copper(II) oxide.

2. Heat the test tube containing copper(II) oxide over the burner at the point where the oxide is placed and observe what happens on the walls of the test tube and on the surface of copper(II) oxide grains. When the colour of the oxide changes stop heating and allow the test tube to cool in the stand.

What substances were formed during heating copper(II) oxide in the hydrogen atmosphere? Write out the reaction equation. What type is the reaction? What property of hydrogen is illustrated by this experiment?

12. Acquaintance with Properties of Hydrochloric and Sulphuric Acids

1. Look at the hydrochloric acid given to you by the instructor. Decide if it has any odour. (Remember the rules for smelling an unknown substance.)

Place about 2 ml of water in a test tube and carefully add about 1 ml of hydrochloric acid. What happens? Has the temperature in the test tube changed? What is the density of hydrochloric acid compared with that of water?

Transfer half the obtained solution to another test tube. Add three drops of litmus to the acid in one test tube and the same amount of methyl orange to the acid in the other test tube. Observe the reaction.

2. Look at the sulphuric acid given to you by the instructor. Decide if it smells of anything (be careful). Incline the test tube slightly. What can you say about *viscosity* of the acid?

Dip a splint into the acid. Remove it carefully and hold over a beaker so that the acid does not drip on the table. What changes in the splint have you noticed?

Place about 2 ml of water in a test tube and add (carefully) about 1 ml of sulphuric acid. Observe the reaction. How does the density of sulphuric acid compare with that of water? Has the acid dissolved in water? Has the temperature of the water changed?

Transfer about half the obtained solution of sulphuric acid into another test tube and add three drops of litmus into one, and the same amount of methyl orange into the other test tube. Observe the reaction.

What are common and what are different properties of sulphuric and hydrochloric acid? Remember the colour of litmus and methyl orange in solutions of the acids.

13. Reaction of Acids with Metals

Place two grains of zinc in two test tubes and add about 1 ml of sulphuric acid into one and the same amount of hydrochloric acid into the other test tube. (Take all precautions when handling the acids.) Take another pair of test tubes and place iron filings in them. Add the same acids to them. Place copper shavings (or copper wire) into the third pair of test tubes and add the acids. If there is no reaction heat slightly the test tube over a burner. (Be careful.)

Note the liberation of gas in some of the test tubes and identify it. Do all metals displace hydrogen from the acids?

14. Reaction of Acids with Metal Oxides

1. Place a small portion of iron(III) oxide in two test tubes and add about 1 ml of sulphuric acid into one, and the same amount of hydrochloric acid into the other test tube. (Take all precautions when handling the acids.) Observe the changes in the test tubes, if any. If no reaction occurs, heat the test tubes slightly over a burner (be careful). Observe the changes. If ferric oxide has dissolved completely, add another portion of the powdered ferric oxide and heat again.

Transfer a few drops of the solution from the test tube in which ferric oxide reacted with sulphuric acid onto a glass plate and evaporate them over a burner. What remains on the glass after evaporation of the liquid?

2. Carry out a similar experiment with the same acids but taking magnesium oxide instead of iron(III) oxide. What do you know now about the response of acids to metal oxides?

15. Solubility of Solids in Water. Variation of Solubility with Temperature

1. Place 0.5 g of potassium nitrate and 0.5 g of sodium chloride into two separate test tubes and add 5 ml of water to each test tube. Mix thoroughly. Have the solids dissolved completely? Add the same substance in small portions to the test tubes where they have completely dissolved until the solid no longer dissolves. Continue stirring the solutions.

Draw your conclusions about the solubility of potassium nitrate and sodium chloride.

2. Heat the test tubes containing saturated solutions of potassium nitrate and sodium chloride one after another to their boiling points (without actually boiling them). If the precipitate of salt on the bottom of the test tube dissolves, add the same salt in small portions until the salt stops dissolving. Has the solubility of each salt changed in the same way with the rising temperature of the solution?

3. Allow the solutions saturated at a temperature close to the boiling point to cool slowly and observe the changes that occur in the solutions of potassium nitrate and sodium chloride. Which salt has precipitated in a greater quantity?

Derive your conclusions about the dependence of solubility on temperature.

16. Acquaintance with Properties of Sodium Hydroxide, Calcium Hydroxide, and Iron(III) Hydroxide

1. Look at the hydroxides of sodium, iron(III) and calcium in test tubes. Describe their aggregation states and colour.

2. Add 3-4 ml of water into each test tube and shake carefully. Is heat liberated in any test tube? Have all three hydroxides dissolved completely? Pass cloudy solutions through a filter.

3. Divide each solution into two parts. Add 2-3 drops of neutral litmus to each of

the three portions (or using a glass rod transfer a drop of each solution on a strip of litmus paper) and add the same amount of phenolphthalein to the remaining three portions. Observe the change in colour.

Fill out the results of your observations in the following form:

Table I.1

Properties of Metal Hydroxides

Name of substance	Formula	State of aggregation	Colour	Solubility in water	Reaction	
					Litmus	Phenolphthalein

17. Neutralization Reaction

1. Place about 5 ml (1/4th test-tube volume) of sodium hydroxide solution into a porcelain dish and add 1-2 drops of phenolphthalein. Observe the change in colour. Add hydrochloric acid from a pipette, first add in 1-2 ml portions and then drop by drop. After adding each new portion stir the solution using a glass rod. When the crimson colour of the solution vanishes from a drop of the acid, stop adding the acid.

2. Transfer about half the solution into a test tube and evaporate the remaining part to dryness over a burner. Use a glass rod to stir the solution during its evaporation. Inspect the obtained salt.

18. Reaction of Insoluble Bases with Acids

Place small amount of copper(II) hydroxide into one test tube and iron(III) hydroxide into another test tube. Inspect the hydroxides. Add sulphuric acid in small portions to the first test tube and hydrochloric acid to the other test tube until the hydroxides dissolve completely. What is the colour of the obtained solutions? Transfer 2-3 drops of the obtained solutions onto glass plates and hold them over the burner to evaporate the liquid. What remains on the plates?

19. Thermal Decomposition of Copper(II) Hydroxide

Place a small portion of cupric hydroxide in a test tube, fix it in the stand in an inclined position with the mouth pointing down, first warm up the entire test tube, and then heat that part where cupric hydroxide is placed. How does the colour of the substance change? What do you observe on the cold walls of the test tube?

Write the results of your observations in the note-book and draw a sketch of the apparatus with the indication of its separate parts and units. Write down the reaction equation.

II. Practical Experiments

Experiment 1. Using Laboratory Burners and a Ring Stand

Using an Alcohol Burner. Structure of Flame

1. *An alcohol burner.* The burner is made up of a reservoir containing alcohol, a wick in a metal tube with a disc, and a glass cap (Fig. II.1).

Remove the glass cap and place the alcohol burner on the bench. Slightly lift the disc and see that nothing interferes with the tight contact of the disc with the edge of the alcohol reservoir neck. This is very important, since otherwise the entire burner may catch light.

2. *Preparing for work.* Prime the burner as follows: pour alcohol into the reservoir through a funnel to about 2/3 its full capacity; pass a cotton wick through the tube so that it will neither be too tight nor too loose. Cut the wick end with scissors. Before lighting the burner, slightly wet the wick with alcohol, and replace the cap. (If a wick is not available, it can be replaced by twisted cotton wool.)

The burner should always be ready for use in the laboratory. When out of use, the burner should always be closed with the cap to prevent evaporation of alcohol.

3. *Lighting a burner.* Only a burning match should be used to light the burner. Never use another burner to light it, because it might cause a fire. Never blow on a burning alcohol burner since this is also dangerous.

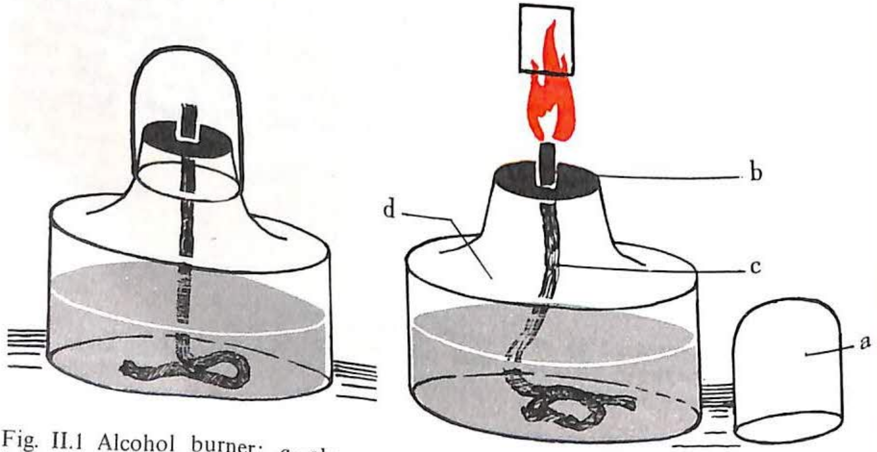


Fig. II.1 Alcohol burner: *a*–glass cap; *b*–tube with a disc; *c*–wick; *d*–alcohol reservoir. The hottest zone of the flame is marked by a frame

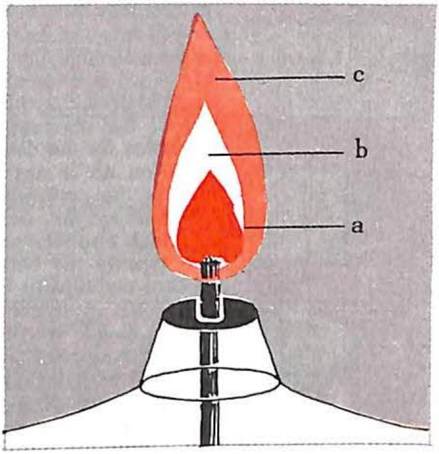


Fig. II.2 The flame of an alcohol burner: *a* – dark 'cold' zone; *b* – luminous hot cone; *c* – less bright but the hottest zone of the flame

In order to extinguish the lit burner it is enough to cover it with the glass cap.

If the size of the flame is smaller than wanted, put out the fire (by replacing the cap) and pull the wick up using the fingers. Light the burner again.

4. *Heating over a burner*. Look at the flame of the burner. Its structure is not uniform (Fig. II.2). The flame is darker in its inner zone over the wick and brighter to the sides and in the upper portion. Quickly put the head of a match inside the darker zone of the flame and hold it there for a while over the wick: it will not catch fire immediately. Now take another match and put its head in the upper zone of the flame: it catches light almost immediately. In what zone of the flame should an object be put if we want to heat it?

Fill a test tube with water to 1/4 its full capacity and heat it in the upper third of the flame. Swing the test tube slightly. See to it that the test-tube bottom does not touch the wick because the test tube may collapse from contact with a relatively cold and wet wick. When water starts boiling, discontinue heating and put down the burner. Glassware of thin (chemical) glass may only be heated over an alcohol burner.

5. Draw a sketch of the alcohol burner and indicate its separate parts in the drawing.

Using a Gas Burner

1. *A Teclu burner*. A Teclu burner comprises a base and a chimney which is screwed into the base (Fig. II.3). Unscrew the chimney from the base and look at the latter. The base is the support of the burner; moreover, gas is delivered through it into the burner. For this purpose the base is provided with a pipe onto which a rubber tube, connecting the burner to the gas mains, is fitted. On the side opposite to the gas inlet pipe there is a screw by which the gas flow into the burner is controlled. If the screw is lightly closed no gas will be delivered into the burner. By releasing the screw one can control the gas flow into the burner.

The chimney has threads in its lower portion by which it can be screwed into the base. An air-inlet adjusting disc is screwed into the base as well. The chimney has a wider portion in its middle part which is covered by a perforated plate through which air is admitted into the chimney to be mixed with the gas. The wider part of the chimney is called a mixer. The intake of air is controlled by the disc. When the disc tightly closes the holes in the mixer air is not admitted into the burner, and conversely, opening the perforations will admit more air.

2. *Preparing for work.* To light a burner act as follows:
(a) attach a rubber tube to the gas cock and its other end to the inlet pipe in the burner's base;
(b) turn the adjusting screw (controlling gas delivery) one or two turns from its initial position (the number of revolutions of the screw depends on the gas pressure in the mains);
(c) lift the air-inlet adjusting disc to its full height: if the burner is lighted with the disc fully open the flame may be blown into the upper part of the chimney. If this happens, turn the gas off immediately and allow the burner to cool. Now close the air inlet and relight the burner.

Prepare a Teclu burner for work independently.

3. *Lighting the burner.* First read the instructions and then proceed to lighting the burner. To light a burner: (a) light

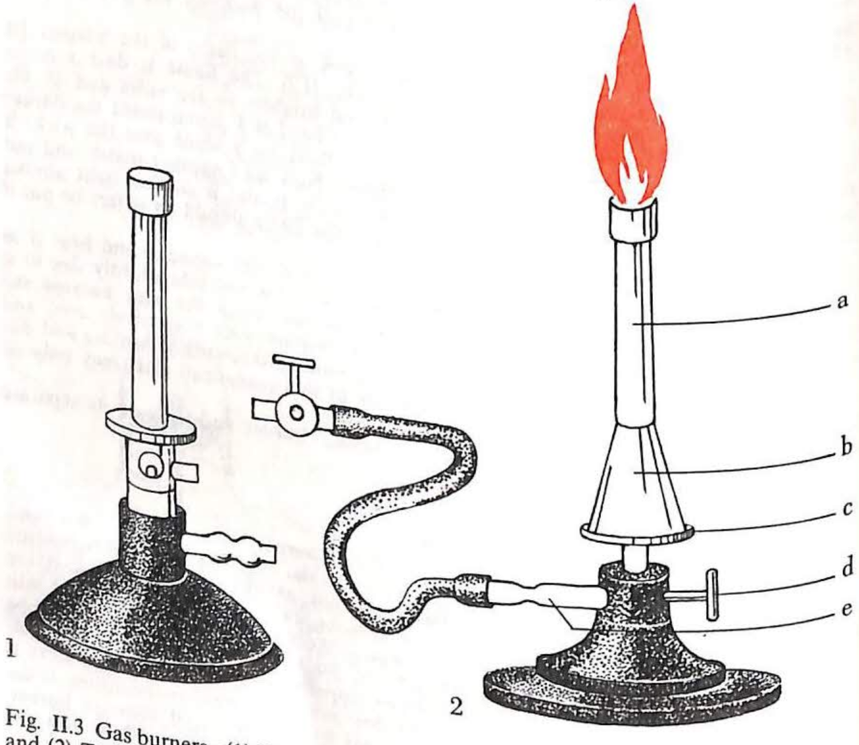


Fig. II.3 Gas burners – (1) Bunsen burner, and (2) Teclu burner: *a* – tube; *b* – mixer; *c* – adjusting disc controlling air intake; *d* – gas adjusting screw; *e* – gas inlet tube

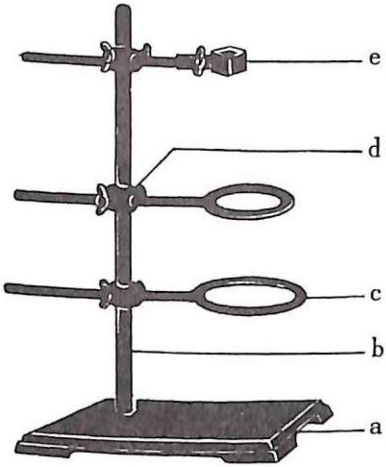


Fig. II.4 Ring stand: *a*–base plate; *b*–upright; *c*–ring; *d*–clamp; *e*–adjustable jaws

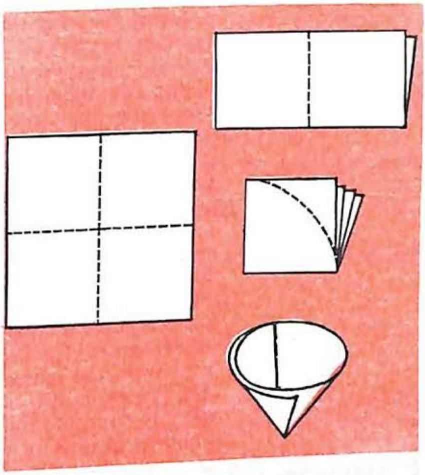


Fig. II.5 Making a filter

a match, (b) open the gas cock, (c) put the burning match to the side of the burner outlet. If the match is put directly over the burner top a strong current of the gas mixture may blow out the burning match; (d) turn the air-inlet disc so that the flame is non-luminous and about 10 cm high.

In order to extinguish the flame, turn off the gas cock. See to it that the gas cock is always closed when the burner is out of use.

4. *Heating over a gas burner.* Pour water into a test tube to about 1/4 its full capacity and hold it in the upper third portion of the flame, slightly swinging it. When the water boils, discontinue heating and turn off the burner.

5. Draw a sketch of the burner and give names to all its component parts.

Using a Laboratory Ring Stand

1. *Design.* The stand (Fig. II.4) is used to hold apparatus during experiments and exercises. The stand comprises a cast-iron base plate (*a*) and an upright (*b*) set into it. The base plate ensures stability of the entire ring stand. Unscrew the upright. Screw in again and always check that the upright is securely screwed into the base plate.

Ring (*c*) and adjustable jaw (*e*) are held in place on the upright by clamps (*d*), which can be moved up and down the upright and also round it. It is enough to undo the fixing screw by which the clamp is held in place on the upright. Fix the clamp in the middle of the upright. Move it up; lower it. Fix the clamp in the middle of the upright again. The ring or the adjustable jaw are fixed into the clamp using another screw. Fix a ring in one clamp and the adjustable jaw in the other.

Since the clamp can be moved up and down the upright and turned to either side, the ring and the adjustable jaws can be arranged at any height and at any required angle toward the vertical and horizontal planes.

2. *Using the ring stand.* Fix a test tube in the jaws so that it assumes the vertical position with the mouth upward. The grip of the jaws on a test tube should be loose enough for the position of the test tube to be readjusted. At the same time the grip should be tight enough for the test tube not to drop out. The grip should not be too tight either because the test tube may break. The test tube should be held by the jaws at its upper portion, near the mouth, not in the middle, because it may prove necessary to heat the test tube along its entire length. Adjust the test tube in the horizontal position. To do so, loosen the fixing screw on the clamp, turn the clamp together with the test tube through an angle of 90°.

Fix a beaker in the ring stand; then fix a porcelain dish. To do so, first place a wire gauze on the ring, and then put the beaker on the gauze. The flame of the burner will heat the gauze and the heat from the gauze will be transmitted to the beaker.

The porcelain dish can be put in the ring without any wire gauze, directly over the flame. The gauze is only used in cases where uniform heating of the dish is required.

Experiment 2. Purification of Table Salt

When doing this exercise you will learn: how to purify a solid from insoluble impurities by one of commonly used techniques, how to make a paper filter, to separate impurities from liquids by filtering, and how to obtain salts from solutions by evaporation.

1. *Dissolution of impure salt.* Place 20 ml of distilled water in a beaker and dissolve the salt by adding it in small portions using a spoon. To accelerate dissolution, stir the liquid using a 'policeman' (a glass rod with a rubber tip). When the salt stops dissolving despite stirring, stop adding the salt. Observe the appearance of the solution.

2. *Purification of an impure solution by filtration.* Porous (blotting) paper is used in the laboratory as the filtering medium. Take a square sheet of paper (the size of which should two times exceed the diameter of the funnel) and fold it in four. Cut a sector using the scissors as shown in Fig. II.5. Unfold the sector to form a cone, and place it in the funnel so that its sides tightly fit the glass walls of the funnel. The tightness depends on the correspondence between the filter and funnel cone angles. The filter should only reach to within 0.5 cm of the funnel's upper edge. Use scissors to cut off any excess paper.

Wetten the filter in the funnel with water. To do so, hold the funnel over a beaker in an inclined position and slightly rotate it. A 'policeman' can be used to transfer water drops onto the filter. The wet filtering paper sticks to the glass walls of the funnel and so ensures the necessary tightness. Place the funnel with the filter in the throat of a flask or in the ring of the stand. In the latter case a beaker should be placed under the funnel stem which should touch the inner walls of the beaker.

Pour the impure salt solution onto a glass rod in the funnel, directing the lower tip of the rod towards the funnel wall (rather than to its centre) as shown in Fig. 1.2. The stream of liquid will then strike the filter paper which tightly rests against the glass. If the liquid stream is directed toward the centre (the vertex of the cone), the filter paper may collapse. The liquid level in the funnel should not rise to more than 0.5 cm above the filter paper margin. If the level rises above the filter margins the liquid will pass between the filter and the funnel walls.

3. *Evaporation of pure solution.* Pour the filtered solution into a porcelain dish and put it in the ring of the stand. Heat the dish over the flame of a burner, stirring the liquid with a glass rod, and make sure that the liquid does not splash from the dish. When crystals start precipitating, stop heating. Compare the salt thus obtained with the salt before it was dissolved.

4. *Make out a report on the experiment using the following plan:*
(1) name of experiment;
(2) name of each step of the experiment with indication of the resultant products;
(3) draw a sketch of the apparatus used in the experiment and name each part of this apparatus;
(4) conclusions.

Experiment 3. Preparing Oxygen and Studying Its Properties

While carrying out this experiment you will check and improve your knowledge of the physical and chemical properties of oxygen. At the same time you will learn how to collect gases in vessels by displacing air from them.

Preparing Oxygen and Collecting It

1. Assemble an apparatus as shown in Fig. II.6. Check it for tightness.
Fill a test tube 1/4 full of potassium permanganate. Put a loose piece of cotton wool in the upper portion of the test tube and close it with a stopper through which a glass tube is passed. Fix the test tube horizontally in the jaws of the ring stand with the bottom of the test tube slightly higher than its mouth. Prepare a bottle with a tightly fitting stopper and put it by the side of the ring stand. First heat the entire test tube and then only that part where potassium permanganate has been placed. Begin heating from the bottom of the test tube and then move the burner toward its mouth, to those portions of potassium permanganate which have not yet decomposed.
Put a glowing splint to the orifice of the gas-outlet tube in order to establish if air has been displaced from the test tube.
2. As soon as oxygen begins issuing from the test tube, lower the end of the outlet tube into the bottle so that it reaches the bottom. Using a glowing splint determine the moment when all air is displaced from the bottle and it contains only oxygen. Remove the outlet tube from the bottle by raising the ring stand. Close the bottle with the stopper, and put aside. Put the ring stand to one side as well.

Burning of Coal in Oxygen

3. Put a piece of charcoal in an iron spoon and heat it in the flame of burner. Put the spoon with the glowing charcoal in the bottle containing oxygen. Observe what happens. When burning stops add lime water to the bottle and shake it. What changes occur in the water? Explain.
4. Write a report of your exercise following the plan given at the end of Experiment 2. Write down the reaction equation in point 2. When giving your conclusions, mention the physical and chemical properties of oxygen that you observed in your experiments.
An assignment to those pupils who have finished their experiments ahead of schedule:

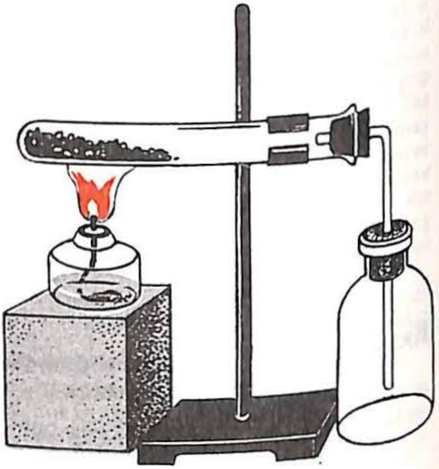


Fig. II.6 Apparatus for preparing and collecting oxygen

Heat potassium nitrate and manganese(IV) oxide to see if oxygen is liberated during this process.

Experiment 4. Preparation of Vitriol Blue by Reaction Between Copper(II) Oxide and Sulphuric Acid

Carrying out this experiment will improve your knowledge of reactions between metal oxides and acids and you will learn how to prepare salts and isolate them from a solution.

1. Write the equation for a reaction between copper(II) oxide and sulphuric acid.
2. Prepare a filter.
3. Transfer carefully about 5 ml of sulphuric acid into a test tube, heat the solution to boiling (taking all precautions), and add about 1/4 of a teaspoonful of copper(II) oxide. Stir the mixture with a glass rod. When copper(II) oxide has dissolved, add another portion of this reagent and stir again until it dissolves. Continue adding the oxide till it stops dissolving. Heat the solution during this procedure but do not allow the solution to boil. To prevent this remove the test tube from the flame from time to time. When a new portion of copper(II) oxide fails to dissolve in the acid, discontinue heating the solution.
4. Pass the hot solution through a filter into a porcelain dish and evaporate until crystals of salt appear. Stop heating, allow the solution to cool down, and observe the crystallization. What is the colour of the crystals?
5. Make out a report of the work done. (Use the plan given above.)

Experiment 5. Preparing Solution of Required Concentration (containing the desired weight fraction of salt)

1. Calculate the weights of water and salt that will be required to prepare a solution of the required concentration.
2. According to your calculations, weigh out on a balance the required weight of salt and measure out distilled water using a volumetric cylinder. (Remember the rules for weighing out

solids and measuring volumes of liquids that you have learnt from the physics lessons.)

3. Place the weighed-out portion of the salt into a flask and add the measured volume of distilled water. Mix the components in the flask until the solid dissolves completely.
4. Write down the formula of the salt and its weight fraction in the prepared solution. Put your note-book alongside the flask.
5. Write a report of the experiment and its results. Write down your calculations in the note-book.

Experiment 6. Experimental Solution of Problems on 'Main Classes of Inorganic Compounds'

In this experiment you will use your knowledge of the theory of classification and properties of oxides, bases, and acids and apply this knowledge to interpretation of practical experiments.

Problem 1. How can an iron nail be cleaned of rust using a chemical method? Carry out the experiment and explain it. Remember that rust contains iron(III) hydroxide.

Problem 2. Obtain a mixture of zinc and copper filings from the instructor. Separate copper filings from the mixture by a suitable chemical method. Write down the reaction equation.

Problem 3. Obtain from the instructor a black powdered mixture. Establish if the mixture contains copper(II) oxide. Write down the reaction equation.

Problem 4. Identify a sodium chloride solution, a solution of an acid, and a solution of an alkali which are contained in three separate test tubes.

Problem 5. Prove experimentally that magnesium hydroxide is a basic hydroxide.

Problem 6. Prove experimentally that magnesium oxide is a basic oxide.

Problem 7. Obtain magnesium sulphate from magnesium oxide.

Problem 8. Obtain iron(III) sulphate from iron(III) hydroxide.

Problem 9. Obtain copper(II) chloride from copper(II) oxide.

Table II.1

Atomic Weights of Important Elements (rounded)

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Aluminium	Al	27	Iron	Fe	56
Antimony	Sb	122	Lead	Pb	207
Arsenic	As	75	Magnesium	Mg	24
Barium	Ba	137	Manganese	Mn	55
Bismuth	Bi	209	Mercury	Hg	201
Boron	B	11	Nickel	Ni	59
Bromine	Br	80	Nitrogen	N	14
Cadmium	Cd	112	Oxygen	O	16
Calcium	Ca	40	Phosphorus	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35.5	Potassium	K	39
Chromium	Cr	52	Silicon	Si	28
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	64	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	88
Gold	Au	197	Sulphur	S	32
Hydrogen	H	1	Tin	Sn	119
Iodine	I	127	Zinc	Zn	65

6 Quantitative Relationships in Chemistry

We have become acquainted with the language of chemistry. We know that the chemical formula of a compound gives much information about this substance and that an equation of a chemical reaction gives much information about the interaction between compounds during a chemical reaction. Chemical equations express not only the qualitative changes that occur during a reaction, but also much quantitative information: they give the weights of the initial reactants and of the resultant reaction products. Below we shall discuss these problems in detail.

6.1 Amount of Substance. Mole

We know that substances react with one another in strictly definite proportions. In order to obtain a pure substance, for example, iron(II) sulphide, the amounts of iron and sulphur taken for the reaction should be such that one iron atom can react with one atom of sulphur.

It is difficult to imagine that the number of atoms or molecules of substances taken for a reaction could be counted. A special physical notion known as the *quantity of substance* is used in chemistry.

Quantity of substance (ν) *is determined by the number of structural units of a given substance* (atoms, molecules, or other objects). The quantity of substance is expressed in *moles* (Latin *moles*, meaning heap or pile).

One mole is the quantity of a substance that contains the number of constituent particles (objects) *equal to the number of atoms contained in 12 g of carbon.* It has been established that 12 g of carbon contain 6×10^{23} atoms. This means that one mole of water contains 6×10^{23} molecules and one mole of sulphur contains 6×10^{23} atoms, etc.

The number 6×10^{23} was determined by an Italian physicist, Amadeo Avogadro. This number (which, more accurately, is 6.022045×10^{23}) is much greater than the total number of hairs on the heads of all the people in the world, and greater than the number of glasses of water contained in all the oceans, seas, lakes, and rivers of the globe. The determination of this number was as important event in chemistry as the determination of the velocity of light in physics.

The use in chemistry of this physical value, the quantity of substance, makes it possible to count the number of objects in this or that portion of a substance and to take substances in proportions required for chemical reactions.

Consider some examples of the practical application of this physical concept.

Example 1. What quantities of aluminium and sulphur are required to prepare aluminium sulphide Al_2S_3 so that all the aluminium and sulphur can react?

The formula Al_2S_3 shows that each pair of aluminium atoms combines with three sulphur atoms to give aluminium sulphide. It follows that two moles of aluminium and three moles of sulphur should be taken for the reaction. These quantities may be increased or decreased proportionally, e. g. 4 moles of aluminium and 6 moles of sulphur, or 0.2 mole of aluminium and 0.3 mole of sulphur, etc.

Example 2. How many atoms are contained in (a) 2 moles, (b) 0.5 mole, and (c) 0.1 mole of sulphur?

Since one mole of sulphur contains 6×10^{23} atoms, (a) two moles of sulphur will contain $2 \times 6 \times 10^{23} = 12 \times 10^{23}$ atoms; (b) 0.5 mole of sulphur, $0.5 \times 6 \times 10^{23} = 3 \times 10^{23}$ atoms; and (c) 0.1 mole of sulphur, $0.1 \times 6 \times 10^{23} = 0.6 \cdot 10^{23}$ atoms.

Example 3. It has been established experimentally that 0.1 mole of aluminium and 0.3 mole of bromine are required to obtain aluminium bromide. Derive the formula of aluminium bromide.

From the condition of the problem it will be seen that 0.1 mole of aluminium reacts with 0.3 mole of bromine, i. e. the quantity of bromine is three times that of aluminium. It follows that one aluminium atom reacts with three atoms of bromine. The formula of aluminium bromide is therefore $AlBr_3$.

?
Δ

1. Why do chemists use the physical notion quantity of substance?
2. What number of molecules is contained in (a) 3 moles, (b) 0.3 mole, and (c) 5 moles of water?
3. What quantities of phosphorus and oxygen are required to prepare phosphorus(V) oxide P_2O_5?
4. To prepare calcium chloride, 0.2 mole of calcium and 0.4 mole of chlorine were reacted. Derive the formula for calcium chloride.

6.2

The Molar Weight

Amounts of substances taken for reactions are measured in moles. How can the required number of moles of a substance be practically measured out? To do this it is necessary to express the weight of substances in grams. *Molar weights* are used for the purpose.

The molar weight of a substance is the relationship between the number of grams of a substance and the number of moles of the same substance.

The molar weight is expressed in grams per mole (g/mol):

$$M = \frac{m}{\nu}$$

where m is the weight in grams, and ν is the quantity of substance in moles.

For example,

$$M(H_2O) = \frac{18\ \text{g}}{1\ \text{mol}} = 18\ \text{g/mol}$$

The molar weight of a substance is constant for each particular substance. For example, the same molar weight of water will be obtained if the ratio of any weight of water to the corresponding number of moles of water is calculated:

$$M(H_2O) = \frac{36\ \text{g}}{2\ \text{mol}} = \frac{9\ \text{g}}{0.5\ \text{mol}} = \frac{1.8\ \text{g}}{0.1\ \text{mol}} = 18\ \text{g/mol}$$

The molar weight of any substance is equal numerically to the molecular weight (i.e. to relative atomic and molecular mass units of atoms and molecules).

Compare:

substance	atomic and molecular weight	relative molecular and atomic weight	molar weight
H_2SO_4	98 amu	98	98 g/mol
P	31 amu	31	31 g/mol
H_2O	18 amu	18	18 g/mol
Cu	64 amu	64	64 g/mol

The weight of a given substance can be calculated from the formula $M = \frac{m}{\nu}$ by the known number of moles, and conversely the quantity of substance in moles can be found from the known weight of this substance.

Example 1. The quantity of copper(II) oxide taken for the reaction is 0.5 mole. What weight of copper(II) oxide should be measured out on a balance?

$M(CuO) = 80\ \text{g/mol};\ \nu = 0.5\ \text{mol};$

$m = M \times \nu;\ m = 80\ \text{g/mol} \times 0.5\ \text{mole} = 40\ \text{g}$

Example 2. An amount of water weighing 36 g is given; determine in moles the quantity of substance it contains.

$$M(H_2O) = 18\ \text{g/mol};\ m = 36\ \text{g};$$

$$\nu = \frac{m}{M};\ \nu = 36\ \text{g} : 18\ \text{g/mol} = 2\ \text{moles}$$

?

△

1. Explain why the numerical values of the weights of atoms of elements and molecules of substances coincide with their molar weights?
2. What do the following notations mean: $m_a(Cu) = 64$ amu; $A_r(Cu) = 64$; $M(Cu) = 64$ g/mol?
3. What do the following notations mean: $\nu(S) = 2$ moles;

$\nu(H_2O) = 0.5$ mole? How can these quantities of substance be expressed in grams?

4. What quantity (in moles) of copper(II) oxide is contained in: (a) 160 g, (b) 16 g, (c) 8 g and (d) 0.8 g?

5. To what weights of iron(III) oxide do the following quantities of substance in moles correspond: (a) 0.25 mole, (b) 3 moles, (c) 0.1 mole, (d) 2 moles?

6. How many molecules do 72 g and 1.8 g of water contain?

7. What number of molecules are contained in 0.5 mole of water?

8. Can 0.5 mole of sulphur be taken instead of 16 g of sulphur for the reaction? Reason your answer.

9. The quantity of a substance required for a reaction was 0.2 mole. A pupil weighed out 6 g of magnesium. Has he fulfilled his assignment? Reason your answer.

■ Drink a cup of water (200 ml) and count the gulps. What quantity of substance does an average gulp of water contain?

6.3 The Molar Volume of Gases. Avogadro's Law

Liquid and solid substances taken in quantities of 1 mole each (Fig. 6.1) occupy comparatively small but different volumes. When solid or liquid substances are converted into gas their volumes sharply increase. But the volume occupied by one mole of any gas will be the same in the same conditions.

In this text-book from now on we shall only deal with volumes of gases measured under standard (normal) temperature and pressure (abbreviated to STP or NTP), which actually are 0°C and atmospheric pressure 760 mm Hg.

Molar volumes of gaseous substances are used in calculations.

The molar volume of gas V_m is the ratio of the gas volume to its quantity in moles. Molar volumes of gases are expressed in litres per mole (l/mol) or in cubic metres per mole (m^3/mol).

The molar volume is constant for all gases taken under normal temperature and pressure; *it is equal to 22.4 l/mol.*

$$V_m = \frac{V}{\nu}$$

where V is the volume in litres and ν is the quantity of substance in moles.

Thus one mole of any substance contains the same number of molecules (or other entities), but unlike solids or liquids, one mole of any gas will also occupy the same volume under the same temperature and pressure.

According to Avogadro, *equal volumes of gases under the same conditions contain an equal number of molecules.*

Why cannot Avogadro's law be extended to solid and liquid substances? The molecules of solids and liquids are brought in close contact with one another and their volumes depend largely on the dimensions of the molecules. When a substance is in the gaseous state, the distance between its molecules is relatively large compared with molecules themselves. The

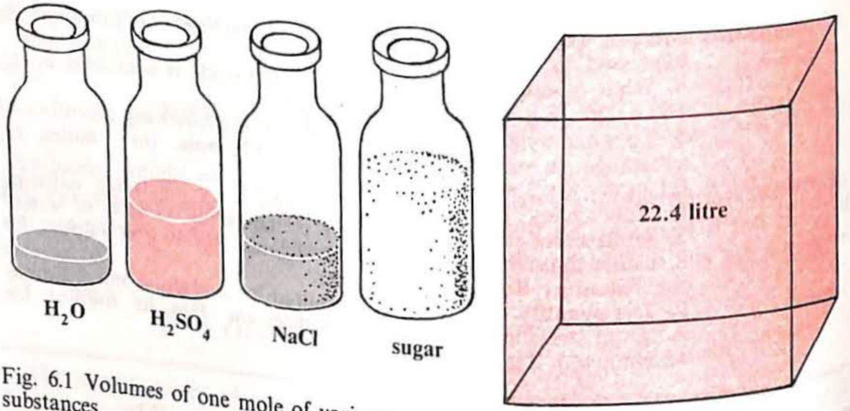


Fig. 6.1 Volumes of one mole of various substances

volume occupied by the molecules of gaseous substances proper is therefore comparatively small.

The volume of a gas is thus determined by the distance between molecules which is about the same in all gases at the same temperature and pressure.

?
Δ

1. Formulate Avogadro's law.
2. What is the molar volume of a gas?
3. Calculate the molar volume of (a) nitrogen (at STP; $\rho = 1.250$ g/litre); (b) methane (at STP; $\rho = 0.719$ g/litre).
4. What volume will (a) 0.5 mole of oxygen, (b) 0.5 mole of hydrogen, (c) 0.5 g of oxygen, (d) 0.5 g of hydrogen, and (e) 0.5 mole of carbon dioxide occupy at STP?

6.4

Relative Density of Gases

If two gases are taken in equal volumes (under the same conditions), they will contain an equal number of molecules but the weights of the gases will be different. Take, for example, oxygen and hydrogen. The weight of oxygen will be as many times greater than hydrogen as the molecular weight of oxygen is greater than the molecular weight of hydrogen, i.e. $32:2 = 16$.

Densities of gases relate as their relative molecular weights

$$\frac{\rho_1}{\rho_2} = \frac{M_{r1}}{M_{r2}}$$

where ρ is density of gas in grams per litre and M_r is relative molecular weight. This ratio is the *relative density of one gas compared to another*. It is designated by the letter D with a subscript denoting the gas relative to which the density of a particular gas is compared. For example, D_{H_2} is the density of a gas relative to hydrogen, and D_{air} is the density of a gas relative to air.

Example 1. Calculate the relative density of carbon dioxide with respect to hydrogen

$$M_r(CO_2) = 44; \quad M_r(H_2) = 2; \quad D_{H_2} = \frac{44}{2} = 22$$

Conversely, once both the density of one gas relative to another, and the molecular weight of the other gas are known, one can *calculate the molecular weight of the gas.*

Example 2. The density of sulphur(IV) oxide relative to air is 32. Calculate the relative molecular weight of sulphur(IV) oxide:

$$M_r(H_2) = 2; \quad D_{H_2} = 32; \quad M_r(SO_2) = 2 \times 32 = 64$$

In practice one often meets with the determination of the density of gases relative to air. Air is a mixture of gases and a 'molecule of air' has no meaning. It is only possible to say that air may have a mean relative molecular weight, which is 29. In order to calculate the density of a gas relative to air, the relative molecular weight of this gas should be divided by 29. Thus, $M_r(CO_2) = 44$, which means

$$D_{air}(CO_2) = \frac{44}{29} = 1.52$$

?

△

1. Calculate the density relative to hydrogen and air of (a) sulphur dioxide SO_2 and (b) water vapour.
2. Calculate the molecular weight and derive the chemical formula of (a) nitrogen if its D_{H_2} is 14, and of (b) phosphorus if D_{H_2} of its vapour is 62.
3. The composition of air in volume per cent is: nitrogen 78, oxygen 21 and argon 1. Calculate (a) quantity of substance in moles, (b) weight of each gas in one cubic metre of air, (c) weight of one cubic metre of air (at STP) and fill in the following table:

Gas	Formula	Molecular weight	Molar weight	%, (v/v)	Quantity, mole	Weight, g
Nitrogen	?	?	?	78	?	?
Oxygen	?	?	?	21	?	?
Argon	?	?	?	1	?	?
Total	—	—	—	100	?	?

6.5 Calculations from Chemical Formulas and Equations

When making calculations from chemical formulas and equations it should be remembered that depending on the conditions of the problem a chemical formula may denote not only one molecule but also one mole of this substance. The formula H_2O not only means a molecule of water with its relative molecular weight of 18 but also a molar weight of water of 18 g/mole and also one mole of water.

Calculations from Chemical Formulas

Example 1. What weight of iron is contained in 40 g of iron(III) oxide? The formula of ferric oxide is Fe_2O_3.

$$M_r(Fe_2O_3) = 2 \times 56 + 3 \times 16 = 112 + 48 = 160$$

$$M(Fe_2O_3) = 160 \text{ g/mol}$$

Since the formula Fe_2O_3 denotes one mole of this substance one can find the weight of Fe_2O_3

$$m = 160 \text{ g/mol} \times 1 \text{ mol} = 160 \text{ g}$$

Let us now calculate the weight of iron contained in the oxide. According to the formula, 160 g of ferric oxide contain 112 g of iron. According to the condition of the problem 40 g of ferric oxide contain x g of iron.

Make out the proportion:

$$160 \text{ g} : 112 \text{ g} = 40 \text{ g} : x \text{ g}$$

whence

$$x = \frac{112 \text{ g} \times 40 \text{ g}}{160 \text{ g}} = 28 \text{ g}$$

(The answer: 40 g of ferric oxide contain 28 g of iron.)

Example 2. What is the weight of some sodium hydroxide if all the sodium atoms in it together weigh 46 g? Calculate:

$$M_r(NaOH) = 23 + 16 + 1 = 40$$

$$M(NaOH) = 40 \text{ g/mol}$$

$$m(NaOH) = 40 \text{ g/mol} \times 1 \text{ mol} = 40 \text{ g}$$

According to the formula, 40 g of sodium hydroxide contain 23 g of sodium atoms. According to the condition of the problem x g of sodium hydroxide contain 46 g of sodium atoms. Make out the proportion:

$$40 \text{ g} : 23 \text{ g} = x \text{ g} : 46 \text{ g}$$

$$x = \frac{40 \text{ g} \times 46 \text{ g}}{23 \text{ g}} = 80 \text{ g}$$

(The answer: Sodium hydroxide weighs 80 g.)

Calculations from Chemical Equations

Example 3. How much (in grams) of Fe_2O_3 is required to prepare 33.6 g of iron by reduction with hydrogen? Solve as follows:

1. Write the reaction equation:

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$$

2. Superscribe the weight 33.6 g of iron above its formula and x g above the formula of ferric oxide. (This is useful because it will now be unnecessary to return later to the condition of the problem in further solution to see

what is given, what is to be found, or in what units of weight of volume.)

$$\begin{array}{llll} x\text{ g} & & 33.6\text{ g} & \\ Fe_2O_3 + 3H_2 & = & 2Fe + 3H_2O & \end{array}$$

3. Determine the molar weights:

$$M(Fe_2O_3) = 160\text{ g/mol};\quad M(Fe) = 56\text{ g/mol}$$

and find the weight of the substances

$$m(Fe_2O_3) = 160\text{ g};\quad m(Fe) = 56\text{ g}$$

4. According to the reaction equation one mole of ferric oxide reacts to give two moles of iron, their weights being 160 g and 112 g, respectively. Subscribe the found weights under the formulas of the substances:

$$\begin{array}{llll} x\text{ g} & & 33.6\text{ g} & \\ Fe_2O_3 + 3H_2 & = & 2Fe + 3H_2O & \\ 160\text{ g} & & 112\text{ g} & \end{array}$$

5. Make out the proportion

$$x\text{ g} : 33.6\text{ g} = 160\text{ g} : 112\text{ g}$$

Solve the proportion:

$$x = \frac{160\text{ g} \times 33.6\text{ g}}{112\text{ g}} = 48\text{ g}$$

(The answer: 48 g of ferric oxide are required.)

Example 4. Determine the volume of hydrogen (at standard temperature and pressure) required to reduce iron from 46 g of ferric oxide.

$$\begin{array}{llll} 46\text{ g} & x\text{ litres} & & \\ Fe_2O_3\ + & 3H_2 & = & 2Fe + 3H_2O \\ 1\text{ mole} & 3\text{ moles} & & \end{array}$$

$M(Fe_2O_3) = 160$ g/mol; $m(Fe_2O_3) = 160\text{ g/mol} \times 1\text{ mol} = 160\text{ g}$ $V_m(H_2) = 22.4\text{ l/mol}$; $V(H_2) = 22.4\text{ l/mol} \times 3\text{ mol} = 67.2$ litre

Subscribe the found weights and volumes under the equation

$$\begin{array}{llll} 46\text{ g} & x\text{ litre} & & \\ Fe_2O_3\ + & 3H_2 & = & 2Fe + 3H_2O \\ 160\text{ g} & 67.2\text{l} & & \end{array}$$

$$160\text{ g} : 67.2\text{ l} = 46\text{ g} : x\text{ litre}$$

$$x = \frac{67.2\text{ l} \times 46\text{ g}}{160\text{ g}} = 19.32\text{ litres}$$

(The answer: 19.32 litres of hydrogen (at STP) are required to reduce iron.)

? △

1. What weights of (a) calcium, (b) carbon, and (c) oxygen are contained in 1 kg of calcium carbonate $CaCO_3$?
2. What quantities in moles of iron are contained in 1 kg of (a) red iron ore Fe_2O_3, and (b) magnetite Fe_3O_4?
3. What weight of sulphur (a) does 1 kg of sulphur(IV) oxide contain, (b) is required to prepare 1 kg of sulphur(IV) oxide?
4. What weights of (a) hydrogen chloride, (b) sulphuric acid, and (c) nitric acid are required to neutralize 20 g of sodium hydroxide?
5. What weight of salt will be produced by the reaction between 28 g of calcium oxide and (a) sulphuric acid, (b) nitric acid, (c) hydrochloric acid?
6. What weight of (a) sulphuric acid, (b) sodium sulphate will be obtained from 40 g of sulphur(IV) oxide?
7. What weights of (a) aluminium, and (b) sulphuric acid are required to prepare 10 g of hydrogen?
8. How many moles and grams of each product will be obtained in the following chain of chemical conversions:

$$Ca \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaCl_2$$

if the weight of the starting calcium is 80 g?

9. What quantity, in grams and moles, of each product will be obtained in the following conversions:
copper(II) hydroxide → copper(II) oxide → copper(II) chloride, if the starting weight of copper(II) hydroxide was 10 g?
10. What quantity, in grams and moles, of each product will be obtained in the following conversions: sulphur → sulphur dioxide SO_2 → sulphurous acid → calcium sulphite, if the weight of starting sulphur is 8 g?
11. What quantity, in grams, of each product will be obtained in the following conversions: iron(III) hydroxide → iron (III) oxide → → iron(III) sulphate, if the weight of the starting ferric hydroxide was 10 g?
12. What quantity, in grams, of iron(III) oxide was spent to prepare what quantities of iron and water if (a) 1 kg of hydrogen, and (b) 1 cubic metre of hydrogen (at STP) were used for reduction of iron?
13. What quantity, in grams, of hydrogen chloride was spent to prepare 1 cubic metre of hydrogen (at STP)?
14. What volume (at STP) of oxygen will be spent to burn 6 kg of coal?

6.6 Volumetric Ratios of Gases

Let us learn how to calculate the volumes of reacting gases taking the reaction between hydrogen and chlorine as an example. The equation of this reaction

$$H_2 + Cl_2 = 2HCl$$

shows that each molecule of hydrogen reacts with a molecule of chlorine to form two molecules of hydrogen chloride. Whatever number of chlorine molecules are used in the reaction the number of hydrogen molecules will be the same, while the number of hydrogen chloride molecules obtained will be two times greater than the number of molecules of each separate gas. According to Avogadro's law the same number of molecules of any gas will occupy the same volume under the same conditions. It means that volume of chlorine reacting with hydrogen is the same as the volume of hydrogen reacting with chlorine, while the volume of the resultant hydrogen chloride will be two times greater.

Thus, if gases react with one another, or if a gaseous product is obtained in the reaction, their volumetric ratios may be found from the reaction equation. The ratios of these volumes will be expressed by coefficients that are put before the formulas. Thus the equation of methane combustion

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

indicates that one volume (1 litre) of methane reacts with two volumes (2 litres) of oxygen to give one volume of carbon dioxide (1 litre). The volume of water obtained in the reaction cannot be determined by Avogadro's law since it holds only for gaseous substances.

The volumes of the reacting and obtained gases are thus proportional to the amounts of these substances

$$\frac{V_1}{V_2} = \frac{\nu_1}{\nu_2}$$

where ν_1 and ν_2 are quantities of substances in moles (they correspond to numerical values of the coefficients in the reaction equation).

Certain calculations can thus be made from reaction equations taking into account the coefficients put before the formulas in the reaction equation.

Example. What volume of oxygen is consumed during combustion of 10 cubic metres of hydrogen?

$$\overset{10\ \mathrm{m}^3}{2H_2} + \overset{x\ \mathrm{m}^3}{O_2} = 2H_2O$$

It will be seen from the reaction equation that hydrogen and oxygen combine in the volumetric ratio of 2 : 1, hence

$$2:1 = 10\ \mathrm{m}^3 : x\ \mathrm{m}^3$$

$$x = 5\ \mathrm{m}^3$$

(The answer: The volume of oxygen that reacts with 10 m^3 of hydrogen during burning is 5 m^3 at STP.)

? 1. Calculate the volume of oxygen required to oxidize 50 litres of carbon(II) oxide. What is the volume of carbon(IV) oxide produced in the reaction?

△ 2. A mixture of 2 litres of chlorine and 3 litres of hydrogen was exploded. Calculate the volume of the hydrogen chloride formed. Which gas and in what volume remains unreacted?

6.6 Volumetric Ratios of Gases

3*. One litre of cyanogen burns to combine with 2 litres of oxygen and to give 1 litre of nitrogen and 2 litres of carbon(IV) oxide. Derive the formula of cyanogen.

6.7

Heat Effect of Chemical Reactions

Chemical reactions are accompanied by liberation or absorption of heat. If energy is absorbed during a chemical reaction, one should provide for an external source that would give the necessary heat for the reaction to occur, and if energy is liberated it should be rationally utilized.

Reactions in which heat is evolved are called exothermic reactions.

Reactions within which heat is absorbed are called endothermic reactions.

In some cases reactions are carried out not to obtain a new product but to utilize heat that is liberated during the reaction. For example, when fuel is burned in furnaces or in the combustion chambers of space rockets, the reaction products are expelled into the air or space. Part of the energy liberated is utilized to propel the spacecraft or rocket. Let us learn how to calculate amounts of heat liberated or absorbed during chemical reactions.

The amount of heat liberated or absorbed during a chemical reaction is called the heat effect of the reaction.

We know from the course in physics that the amount of heat is expressed in Joules and can be measured by a calorimeter. Consider an example. Burn 1 g of coal in a calorimetric bomb and measure the amount of heat liberated. This will be 33.5 kJ. One mole of carbon weighing 12 g burns to evolve 402 kJ. Write this value in the right part of the equation describing the reaction of coal burning:

$$C + O_2 = CO_2\uparrow + 402\ \text{kJ}$$

The sign "+" put before the value expressing the heat effect of the reaction shows that heat is liberated. If the reaction is endothermic heat effect is put in the left part of the equation or it may be written in the right part with the sign reversed. The reaction of water decomposition will be written as this

$$2H_2O + 571.6\ \text{kJ} = 2H_2 + O_2$$

or

$$2H_2O = 2H_2 + O_2 - 571.6\ \text{kJ}$$

Equations of chemical reactions in which heat effect Q is indicated are called *thermochemical equations.*

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* Answers to problems marked with an asterisk are given at the end of the text book (page 225).

If we have a certain store of a substance that may react to evolve heat, we may say that we have a certain amount of energy in store. This is called chemical energy. It is part of the internal energy of substances which does not exhibit itself until a chemical reaction begins. Latent energy, contained in reactants and liberated from them during a reaction, is transmitted to other substances in the form of a certain amount of heat. In some cases, for example during an explosion of dynamite, it often converts into mechanical energy, and in a voltaic cell and storage batteries it is converted into electric current. In all these cases the law of conservation of energy is always fulfilled.

Example 1. Make out a thermochemical equation for a reaction of obtaining water from the simple substances.

This reaction is reverse of decomposition of water. The parts of the equation should therefore change places. Write the heat effect in the right part of the new equation and change the 'minus' sign for 'plus':

$$2H_2 + O_2 = 2H_2O + 571.6\ \text{kJ}$$

Example 2. What amount of heat will be evolved during burning of 1 kg of coal?

Write a thermochemical equation of the reaction:

$$\underset{12\ \text{g}}{\overset{1000\ \text{g}}{C}} + O_2 = CO_2 + \overset{x\ \text{kJ}}{402\ \text{kJ}}$$

Superscribe the values given in the condition of the problem above the symbol C (1 kg = 1000 g), x kJ (the sought value) over the heat effect, and subscribe the weight of one mole of carbon, i.e. 12 g, under the symbol C. Now make out the proportion

$$x : 402\ \text{kJ} = 1000\ \text{g} : 12\ \text{g}$$

whence

$$x = 335\,000\ \text{kJ}$$

Example 3. The thermochemical equation of methane burning is

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 892\ \text{kJ}$$

What volume of oxygen (at STP) is spent during burning of methane if 4187 kJ of heat are liberated during this process?

Superscribe the value given in the condition of the problem above the heat effect of the reaction (4187 kJ) and x litres above the formula of oxygen (the sought value), superscribe the volume (in litres of oxygen at STP) which can be found from the formula

$$V = V_m \times \nu; \quad 22.4\ \text{litre/mol} \times 2\ \text{mol} = 44.8\ \text{litres}$$

$$CH_4 + \underset{44.8\ \text{litres}}{\overset{x\ \text{litres}}{2O_2}} = CO_2 + 2H_2O + \overset{4187\ \text{kJ}}{892\ \text{kJ}}$$

$$x\ \text{litres} : 44.8\ \text{litres} = 4187\ \text{kJ} : 892\ \text{kJ}$$

whence

$$x = 210 \text{ litres.}$$

?

△

1. The thermochemical equation of the reaction by which mercury oxide is formed is

$$2Hg + O_2 = 2HgO + 168 \text{ kJ}$$

Write the thermochemical equation for the reaction of decomposition of mercury oxide.

2. What volume of methane (at STP) should be burnt to evolve 8374 kJ of heat?

3. What amount of heat has been liberated during combustion of methane if it is known that 16 g of oxygen have been spent in the reaction?

4. What volume (at STP) of oxygen has been spent to burn coal if it is known that 2010 kJ of heat have been evolved?

5. Write a thermochemical equation for the reaction by which quicklime is obtained

$$CaCO_3 = CaO + CO_2 - 180 \text{ kJ}$$

The heat required to maintain the reaction is provided by burning coal in a furnace. What is the minimum amount of coal needed to prepare one ton of quicklime?

6. Using the equation

$$S + O_2 = SO_2 + 297 \text{ kJ}$$

calculate the amount of heat that will be evolved (a) during combustion of 1 kg of sulphur, (b) during preparation of 1 kg of sulphur dioxide, and (c) when obtaining 1 litre (at STP) of sulphur dioxide.

7. Using the thermochemical equations

$$2Cu + O_2 = 2CuO + 276 \text{ kJ}$$

$$3Fe + 2O_2 = Fe_3O_4 + 1118 \text{ kJ}$$

calculate the amount of heat that is liberated (a) during oxidation of 1 kg of each metal, (b) during formation of 1 kg of metal oxide.

8. Using the following thermochemical equations

$$H_2 + Cl_2 = 2HCl + 184 \text{ kJ}$$

$$H_2 + Br_2 = 2HBr + 71 \text{ kJ}$$

$$H_2 + I_2 = 2HI - 50 \text{ kJ}$$

calculate the amounts of heat that are evolved or consumed if it is known that: (a) 1 litre (at STP) of hydrogen has reacted, and (b) 1 litre (at STP) of hydrogen halide has been obtained in each reaction.

7

Periodic Law and Periodic System of Chemical Elements by D. I. Mendeleev

7.1 First Attempts of Classification of Chemical Elements

Each science begins with the accumulation of facts. The more facts are available, the stronger the necessity arises to classify them. It would be difficult to deal with the wealth of the animal and plant kingdom on Earth if scientists had not sorted similar animals and plants into their natural families. The first attempts to classify factual data usually were a failure. For example, animals were first classified by their habitat (water and earth) or by their appearance. According to such classification, whales were attributed to the class of fishes despite their anatomical structure.

Zoology studies animals and chemistry deals with types of atoms or chemical elements. The world of chemical elements is varied as well. The chemical elements total 107 at the present time. What properties of chemical elements are used for their classification?

The first classification of chemical elements was also based on the apparent properties of the elements. Thus only metals and nonmetals were distinguished. Let us remember their characteristic properties.

Metals in the free state are characterized by a metallic lustre, they readily conduct electricity and heat. Nonmetals conduct electricity or heat poorly, nor have they (as a rule) metallic lustre. Metals and nonmetals differ in their chemical properties too: hydroxides of typical metals are bases while hydroxides of nonmetals are acids. Metals do not form volatile compounds with hydrogen while nonmetals do.

At the same time there is a group of elements that have both metallic and nonmetallic properties. Nonmetal iodine, for example, looks very much like a metal when it is in the free state. It has some of the physical properties of metals and even conducts electricity. Zinc is another element that has both metallic and nonmetallic properties. According to the physical properties it is a metal, but let us study the chemical properties of its hydroxide. Place a suspension of zinc hydroxide in a test tube and add hydrochloric acid. The precipitate dissolves because a soluble salt $ZnCl_2$ is formed by this reaction. Zinc hydroxide behaves like a base in this reaction. Place zinc hydroxide precipitate in another test tube and add sodium hydroxide solution. The precipitate dissolves. This indicates that zinc hydroxide has reacted with the alkali to form a water-soluble compound Na_2ZnO_2. Compare this formula with the formula of zinc hydroxide: you will see that sodium has been substituted in zinc hydroxide for hydrogen. But hydroxides which react with alkali to exchange their hydrogen for metal are known as acids. This means that zinc hydroxide behaves like an acid in its reaction with sodium hydroxide. Its formula can therefore be written $Zn(OH)_2$ or H_2ZnO_2. The reaction of zinc hydroxide with sodium hydroxide can be expressed as follows:

$$H_2ZnO_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Zinc hydroxide has thus the properties of a base when it reacts with acids and the properties of an acid when it reacts with alkalis.

Hydroxides that exhibit the properties of both bases and acids are called amphoteric.

Aluminium hydroxide and hydroxides of some other metals also have amphoteric properties. Oxides of these elements (ZnO and Al_2O_3) are also amphoteric. They react both with acids and alkalis to form water and the corresponding salts.

The amphoteric character of the hydroxides and oxides of these elements shows that they occupy an intermediate position between typical metals whose hydroxides and oxides exhibit only properties of basic oxides and bases, and nonmetals whose hydroxides and oxides have only the properties of acids and acidic oxides.

Classification of elements into metals and nonmetals is thus imperfect (like the above-mentioned first classification of animals).

Among chemical elements, just as among animals and plants, there are families which unite the elements with similar properties in smaller groups. You have already acquainted yourselves with one such family. This is the family of inert gases. Unlike all other nonmetals, inert (noble) gases do not form compounds with hydrogen or metals, in other words their valency with respect to these elements is zero. Molecules of the inert gases are monatomic: He, Ne, Ar, Kr, Xe.

Now you will become acquainted with two more natural families of elements: one of them includes elements with vivid metallic properties and the other with nonmetallic properties.

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1. Describe the properties of (a) typical metals, (b) typical nonmetals.
2. Prove that there is no distinct boundary line between metals and nonmetals.
3. Describe physical and chemical properties of the noble gases.

7.2 Alkali Metals and Halogens

When you studied water you become acquainted with a metal that was very much unlike those substances that you would normally call a metal. This was sodium. Its chemical symbol is Na, and its atomic weight is 23. Sodium is lighter than water, it easily melts, it is ductile and soft. Like all metals sodium has a metallic lustre and it readily conducts heat and electric current. These are the physical properties of sodium.

One chemical property of sodium you already know: its high reactivity toward water. It replaces hydrogen in water to form sodium hydroxide

$$2Na + 2H_2O = H_2\uparrow + 2NaOH + Q$$

When heated in air sodium melts, and burns with flames to form (among other reaction products) sodium oxide Na_2O. Sodium oxide is a basic oxide. When combined with water it forms the hydroxide NaOH which is soluble in water. Its solution in water is alkali.

Sodium is univalent in all its compounds.

There are five other metals that resemble sodium. These are lithium Li, potassium K, rubidium Rb, cesium Cs, and francium Fr. The simple substances of these elements have a low density, they are elastic, light and ductile, they easily melt and burn, and all react with water, displacing hydrogen from it. Like sodium, all these metals are univalent. Their compounds are therefore similar in structure:

oxides	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
hydroxides	LiOH	NaOH	KOH	RbOH	CsOH

All these compounds have similar properties. Like sodium hydroxide, their hydroxides are alkalis. The six metals are therefore known as the *alkali metals*. Of all metals, the alkali metals are the most active chemically while their hydroxides are the strongest alkalis.

But the alkali metals also differ in their properties. Their densities, their melting and boiling points, and their chemical activities are different. Let us

Table 7.1

Physical Properties of the Alkali Metals

Name and symbol	Atomic weight	Melting point, °C	Boiling point, °C	Density, g/cm³
Lithium Li	6.9	179	1370	0.53
Sodium Na	23.0	97.8	883	0.97
Potassium K	39.1	63.6	760	0.85
Rubidium Rb	85.5	39.0	696	1.52
Cesium Cs	132.9	28.6	685	1.87

Table 7.2

Chemical Properties of the Alkali Metals

Name and symbol	Atomic weight	Burning conditions	Oxidability in air	Formulas of hydroxides and variation in their properties	
Lithium Li	6.9	Ignites on heating	Increases ↓	Solubility increases ↓	LiOH
Sodium Na	23.0				NaOH
Potassium K	39.1	Ignites at 20-25°C			KOH
Rubidium Rb	85.5				RbOH
Cesium Cs	132.9				CsOH

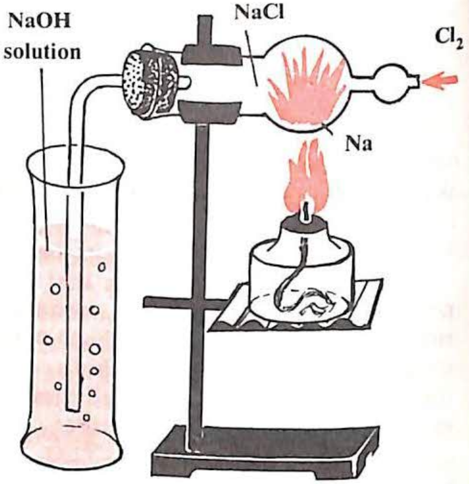

Fig. 7.1 Burning sodium in chlorine

arrange the alkali metals in the order of their increasing atomic weights and compare their physical (Table 7.1) and chemical (Table 7.2) properties.

Pay attention to the regular change in the physical and chemical properties of the alkali metals: this is probably explained by the variation in the structure of their simple substances with increasing atomic weight of the elements.

The alkali metals are chemical elements with a most pronounced metallic character. Now consider the elements in which the nonmetallic properties are most noticeable. Chlorine (chemical symbol, Cl, the atomic weight, 35.5) is among them. You already know some chlorine compounds. These are hydrochloric acid HCl and sodium chloride NaCl.

The chlorine molecule is diatomic. Hence its formula, Cl_2. Chlorine derives its name from the Greek *chloros*, light-green. This is a heavy greenish gas with a pungent odour.

Let us first study the chemical properties of chlorine which are demonstrated in chemical reactions with metals. Consider its reaction with sodium. Molten sodium burns in chlorine to form a white smoke which consists of minutest crystals of sodium chloride (Fig. 7.1):

$$2Na + Cl_2 = 2NaCl + Q$$

Chlorine combines with almost all metals. It even reacts with hydrogen to give a colourless gas hydrogen chloride

$$H_2 + Cl_2 = 2HCl + Q$$

A solution of hydrogen chloride in water has acid properties and is already known to you as hydrochloric acid.

In its compounds with hydrogen and metals chlorine is always univalent.

As sodium represents the family of the alkali metals, so chlorine is representative of the family of the halogens, the nonmetals that have similar properties. Apart from chlorine, the halogen group also includes fluorine F, bromine Br, iodine I, and astatine At. The physical property which is common to all the halogens is their volatility. The common chemical property of the halogens is high activity toward metals and hydrogen. They all combine with hydrogen and metals and are always univalent in these compounds. The compounds of the different halogens with one and the same element are therefore of similar composition:

HF	HCl	HBr	HI	HAt
NaF	NaCl	NaBr	NaI	NaAt
AlF_3	$AlCl_3$	$AlBr_3$	AlI_3	$AlAt_3$

These compounds have similar properties. Hydrogen halides (the compounds of the halogens with hydrogen) are volatile and their aqueous solutions are acids. Metal halides (the compounds of the halogens with metals) are salts. Hence the name halogens which in Greek means giving birth to salts (*halos* salt + *genes* born).

Alongside these similarities, the molecules of halogens also have differing properties: their state of aggregation under normal conditions, their colour, and their chemical activities are all different. The properties of the halogens vary regularly with the increasing atomic weight of the element (see Table 7.3).

Table 7.3

Variation of Properties of the Halogens

Name and symbol	Atomic weight	Formula of simple substance	State of aggregation at STP	Colour	Boiling point, °C	Density, g/cm^3
Fluorine F	19.0	F_2	Gas	Light-green	−188	1.1 (in liquid state)
Chlorine Cl	35.5	Cl_2	Gas	Yellowish-green	−34	1.57 (in liquid state)
Bromine Br	79.9	Br_2	Liquid	Brown-red	59	3.14
Iodine I	127	I_2	Solid (crystals)	Dark-grey	185	4.94

Now compare the chemical activity of the halogens toward hydrogen. The heat effect of the reaction between hydrogen and the halogens decreases with increasing atomic weight:

$$H_2 + F_2 = 2HF + 251 \text{ kJ}$$
$$H_2 + Cl_2 = 2HCl + 184 \text{ kJ}$$
$$H_2 + Br_2 = 2HBr + 71 \text{ kJ}$$
$$H_2 + I_2 = 2HI - 50 \text{ kJ}$$

One mole of hydrogen reacts with one mole of fluorine (the halogen with the least atomic weight) to evolve the maximum amount of heat, while iodine reacts with hydrogen to absorb energy instead of liberating it, and the 'plus' sign is reversed for 'minus'. Stability of the hydrogen halides decreases accordingly. Hydrogen iodide, for example, is so unstable that it partly decomposes into hydrogen and iodine when a hot glass rod is introduced into it. Violet iodine vapour appears as the sign of the reaction.

The chemical activity of the halogens toward metals and hydrogen falls with increasing atomic weights of the elements. The most active halogen is fluorine. Moreover, it is not only the most active halogen but the most active of all nonmetals.

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1. By what common properties are the alkali metals united into one natural family of chemical elements?
2. How do (a) physical properties of the alkali metals in the free state, (b) their chemical properties, and (c) solubility of their hydroxides, change with the increasing atomic weights of the alkali metals?
3. What are the properties of an artificially prepared element francium (at. wt., 223), which is also an alkali metal? Will it sink or float in water? What is its response to water or oxygen? (Write the equation for its reaction with water.) What are the formula and properties of its hydroxide? Write the formula of francium sulphate.
4. Explain how the properties of (a) the alkali metals and (b) the halogens change with the increasing atomic weights of these elements. (Consult Tables 7.1, 7.2, and 7.3, respectively.)
5. Describe the chemical properties of chlorine. Give equations for the reactions characteristic of chlorine.
6. Write the equations for reactions by which zinc chloride can be prepared by the four methods already known to you.
7. How do the physical properties of the halogen molecules change with the increasing atomic weights of the elements?
8. What are the common properties of the halogen molecules?
9. How do the chemical properties of the halogens change with the increasing atomic weights of the elements?
10. Describe the reaction of addition between aluminium and bromine, aluminium and iodine.
11. Describe the physical and chemical properties of hydrogen halides (compounds of the halogens with hydrogen).
12. Using the following thermochemical equations

$$\begin{aligned} 2\text{Na} + \text{F}_2 &= 2\text{NaF} + 1139\ \text{kJ} \\ 2\text{Na} + \text{Cl}_2 &= 2\text{NaCl} + 821\ \text{kJ} \\ 2\text{Na} + \text{Br}_2 &= 2\text{NaBr} + 720\ \text{kJ} \\ 2\text{Na} + \text{I}_2 &= 2\text{NaI} + 569\ \text{kJ} \end{aligned}$$

calculate the amounts of heat that will be evolved in each case if the following quantities of the reactants are taken: (a) 1 g of halogen, (b) 1 g of sodium, (c) 1 cm^3 of sodium.

Note: to solve the latter problem, consult Table 7.1 on p. 131

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Make 18 cards as shown in Fig. 7.2. Write below the symbol of the chemical element, its atomic weight, its valency in the higher oxides, and below that, its valency in the volatile hydride (if such a hydride exists). Draw a blue line on cards with metals, a red and a blue lines

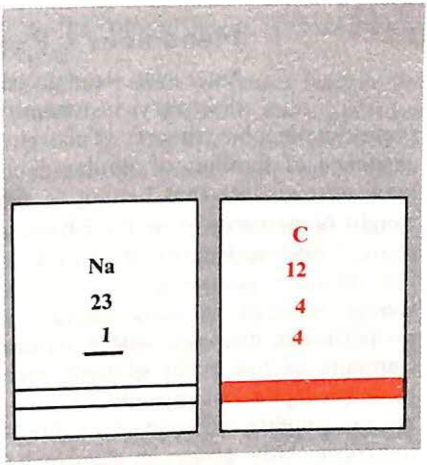

Fig. 7.2 Cards

Table 7.4

Element	Symbol	Atomic weight	Valency in		Note
			higher oxide	hydrogen compound	
Aluminium	Al	27	3	—	amphoteric hydroxide
Argon	Ar	40	0	?	?
Beryllium	Be	9	2	—	amphoteric hydroxide
Boron	B	11	3	—	nonmetal
Carbon	C	?	4	4	nonmetal
Chlorine	Cl	35	?	?	?
Fluorine	F	19	—	?	?
Helium	He	4	0	?	?
Hydrogen	H	?	?	—	?
Lithium	Li	7	?	—	?
Magnesium	Mg	24	2	—	?
Neon	Ne	20	0	?	?
Nitrogen	N	14	5	3	nonmetal
Oxygen	O	?	—	?	?
Phosphorus	P	31	5	3	nonmetal
Silicon	Si	28	4	4	nonmetal
Sodium	Na	23	?	—	?
Sulphur	S	32	6	2	?

on cards where the hydroxide is amphoteric, and a red line on cards with nonmetals. Use any special symbols you may choose to mark the cards with the alkali metals, the halogens, and the noble gases. When filling in the cards, consult Table 7.4. Fill in the necessary data instead of the question marks. For the next lessons prepare another card for beryllium and fill in the atomic weight, followed by a question mark, of 13.5 (?), likewise a valency of 3 (?).

7.2 Alkali Metals and Halogens

7.3

Mendeleev's Periodic Law

Now we are prepared for acquaintance with the great discovery in chemistry which comes only second to the atomic-molecular theory. This is the periodic law of Mendeleev. The existence of families of similar elements led Mendeleev to search for links between elements that belong to different families. He assumed the atomic weight of elements to be their basic property which, unlike valency, does not change, and he decided to find the general law that would explain changes in the chemical properties of elements by variation in their atomic weights. Remember that we have already dealt with such regular changes in the properties of elements within natural families. To do that we arranged the elements in the order of their increasing atomic weights. Let us use this principle again: arrange all chemical elements in the order of their increasing atomic weights beginning with the element with the least atomic weight, i.e. hydrogen. Now give each element its own number in the order in which they are arranged in Table 7.5. The number assigned to each element in this table is called the *atomic number*.

Table 7.5

Element	Atomic number	Symbol	Atomic weight (rounded)	Oxide	Valency in higher oxide	Volatile hydride	Valency in hydride
Hydrogen	1	H	1	H_2O	1		—
Helium	2	He	4	—	0		—
Lithium	3	Li	7	Li_2O	1		—
Beryllium	4	Be	9	BeO	2		—
Boron	5	B	11	B_2O_3	3		—
Carbon	6	C	12	CO_2	4	CH_4	4
Nitrogen	7	N	14	N_2O_5	5	NH_3	3
Oxygen	8	O	16	—	—	H_2O	2
Fluorine	9	F	19	—	—	HF	1
Neon	10	Ne	20	—	0	—	0
Sodium	11	Na	23	Na_2O	1		
Magnesium	12	Mg	24	MgO	2		—
Aluminium	13	Al	27	Al_2O_3	3		—
Silicon	14	Si	28	SiO_2	4	SiH_4	4
Phosphorus	15	P	31	P_2O_5	5	PH_3	3
Sulphur	16	S	32	SO_3	6	H_2S	2
Chlorine	17	Cl	35	Cl_2O_7	7	HCl	1
Argon	18	Ar	40	—	0		0

Chemical elements belonging to one natural family do not follow one another in this series, but occur in a certain sequence. Let us divide the obtained series into groups each of which begins with an alkali metal. Consider the first group that begins with lithium (No. 3) and ends with neon

(No. 10). Note the changes that occur in the properties of the chemical elements with their increasing atomic weight.

First consider valency. Their valency in higher oxides increases from 1 (in lithium) to 5 (in nitrogen), while the valency in their volatile hydrides (compounds with hydrogen) decreases from 4 (in carbon) to 0 (in neon), because neon is known as the inert element that does not react with hydrogen.

How are metals and nonmetals placed in this little series? It begins with an alkali metal, which is representative of the elements with most pronounced metal properties. These properties become less marked in beryllium whose hydroxide is amphoteric, and become nonmetallic in boron. The other five elements are also nonmetals. Their nonmetallic properties gradually increase until they are most pronounced in fluorine, the representative of the halogens. But strengthening of the nonmetallic properties discontinues with fluorine and the last place in the series is occupied by neon, the representative of the inert elements.

Consider the elements that come after neon. The eleventh element is sodium. Like lithium it is an alkali metal and its valency is 1. As we pass from sodium to magnesium and further to aluminium up to chlorine, the valency of the elements in their higher oxides increases by one unit from 1 (in sodium) to 7 (in chlorine), while the valency in volatile compounds with hydrogen (hydrides) decreases from 4 (in silicon) to 1 (in chlorine), which is followed by argon, noble gas, whose valency with respect to hydrogen is 0.

The metallic character which is most pronounced in sodium decreases in magnesium and even more so in aluminium whose hydroxide is amphoteric. Silicon which comes next is a nonmetal. The nonmetallic properties are strengthened in phosphorus and sulphur and attain their maximum in chlorine, the representative of the halogens.

Variation of properties in the elements can easily be illustrated by simple experiments with compounds containing these elements.

If we burn a piece of sodium, powdered magnesium, aluminium, silicon, phosphorus or sulphur we obtain white powders of the oxides Na_2O (and oxides of other composition), MgO, Al_2O_3, SiO_2, P_2O_5. Sulphur forms two oxides, namely SO_2, a gas with a pungent odour, and SO_3 (in the presence of ferric oxide as a catalyst). The oxides so formed dissolve in water. If we test these solutions with litmus paper we shall identify alkali in the first test tube (where sodium was burnt), a weak alkali solution in the second test tube (burnt magnesium), and acid in the fifth test tube where phosphorus was burnt. The oxides of aluminium and silicon are insoluble in water, but aluminium oxide dissolves in acids and alkalis (an amphoteric oxide). Silicon oxide can react with alkalis (acidic oxide). Chlorine does not react with oxygen directly but it has a higher oxide, with the formula Cl_2O_7, which dissolves in water to give an acid with the composition $HClO_4$.

Thus, the properties of the elements from lithium to neon and from sodium to argon change in a similar way with their increasing atomic weights:

(1) metallic properties weaken;

(2) nonmetallic properties strengthen;
(3) valency increases in higher oxides;
(4) valency decreases in corresponding hydrides (hydrogen compounds with nonmetals);
(5) the properties change from basic, through amphoteric, to acidic.

We can now conclude that the chemical properties of the elements change regularly with their increasing atomic weights. In other words, the properties recur periodically in subsequent elements.

Mendeleev discovered his periodic law in 1869 and formulated it as follows: "The properties of simple substances as well as the forms and properties of compounds of elements vary periodically with the atomic weight of the elements."

Regularity of changes in the properties of the elements from lithium to argon is especially pronounced if we arrange the two series one beneath the other:

	Li	Be	B	C	N	O	F	Ne
atomic number	3	4	5	6	7	8	9	10
	Na	Mg	Al	Si	P	S	Cl	Ar
atomic number	11	12	13	14	15	16	17	18

Both series begin with the alkali metals and end with the inert elements. The elements with similar properties, for example, the alkali metals Li and Na, the halogens F and Cl, the inert gases Ne and Ar are all arranged one beneath the other.

Series of elements arranged in the order of their increasing atomic numbers, beginning with an alkali metal and ending with an inert gas, are called periods.

If we arrange periods one beneath the other we shall have the periodic table of chemical elements, which is a graphic representation of the periodic law (see plate I on page 226).

Let us continue with our discussion of the periodic table. The element which comes next to argon should begin a new period, and it should therefore be an alkali metal. This is potassium. But contrary to our expectations, the atomic weight of potassium is slightly lower than that of argon. If we continue arranging the chemical elements in the order of their increasing atomic weights, we shall have to change the places of argon and potassium and so break the regular periodicity: neither potassium nor argon would then stand in the group of elements with similar properties. The alkali metal potassium would stand in the column of the noble gases while argon would be found in the column where the alkali metals stand. Therefore we disregard the atomic weights and place argon where it belongs, i.e. in the column of the inert gases where it is assigned the atomic number of 18. Potassium, despite its lower atomic weight, is assigned the atomic number of 19 and is placed in the column of the alkali metals.

There are three other pairs of adjacent elements in which the atomic weights and the atomic numbers do not obey the general law of periodicity. These four exceptions show that the properties of chemical elements depend to a greater extent on the atomic number than on their atomic weights. How do the properties of the elements depend on the atomic number?

From our physics course we know that atoms consist of a positively charged nucleus and negatively charged electrons that rotate around the nucleus. The atom on the whole is a neutral entity since the positive charge of the nucleus is counterbalanced by the negative charge of the electron shell (the summary charge of the electrons rotating round the positively charged nucleus).

The charge of the atomic nucleus of each chemical element is equal numerically to the atomic number of the element which is assigned to it in the periodic table. We assume the charge of one electron to be 1. Hence the number of electrons that form the electron shell of the atom is equal to the atomic number of the element. The atom of hydrogen, the first element in the periodic table, consists of the nucleus bearing the positive charge $+1$ and one electron with the charge -1. The atom of helium, the second element, has a dipositive nucleus and two negatively charged electrons, etc. The charges of the atomic nuclei of those elements which, like potassium and argon, occupy 'improper' places in the periodic table, appeared to equal the atomic numbers 'unlawfully' given in the periodic table. In other words, *the atomic number of a chemical element is equal numerically to the charge of the nucleus of its atom.*

At the present time the periodic law of Mendeleev is formulated as follows:

The properties of chemical elements change periodically depending on the charge of their atomic nuclei.

As a rule, atomic weights increase with the charge of the atom nucleus. The periodic law was therefore discovered by Mendeleev by considering the atomic weights of the elements, the only quantitative characteristic of elements that was then known.

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1. Formulate the periodic law.
2. What is a period? How do the properties of chemical elements change within the periods with their increasing atomic number?
3. What is the physical meaning of the atomic number of a chemical element?

7.4

Structure of the Nucleus

The nucleus is a part of the atom. The question arises whether or not the atomic nucleus is actually indivisible? Or can it be further divided into smaller components?

Chemical elements with very high atomic numbers are radioactive. They incessantly decompose to emit alpha (α) and beta (β) particles. Beta particles are electrons.

Alpha particles are heavier than electrons, and they are charged positively. This means that they can only be emitted by the nuclei of the atoms, and this in turn indicates that the atomic nuclei also have a complicated structure. What is this structure? Alpha particles move at a very fast speed and are capable of destroying the atomic nuclei with which they collide. Such a bombardment of the atomic nuclei with alpha particles gives birth to new particles, *protons* and *neutrons*.

A proton is a particle with a positive charge + 1 and a mass equal to that of the hydrogen atom, i.e. about 1 amu. Protons thus form the nuclei of hydrogen atoms. Neutrons are particles whose mass is also about 1 amu but they bear no charge. Nuclei of all atoms consist of protons and neutrons. Because neutrons are not charged the charge of the nucleus is determined by the number of protons contained in it. The number of protons in a nucleus is therefore equal to the charge of the nucleus, i.e. the atomic number of the element. The mass of the atom is determined by the total mass of the component particles, protons and neutrons. The mass of protons and neutrons is approximately the same, i.e. about 1 amu. Hence the number of neutrons in an atomic nucleus should be equal to the difference between the atomic weight rounded to a whole number and the atomic number of the element. The atomic weight of the potassium, for example, is 39 amu, while its atomic number is 19. The total number of protons and neutrons composing the nucleus of the potassium atom is therefore 39. The nucleus of the potassium atom is known to contain 19 protons. The number of neutrons will then be $39 - 19 = 20$. The atomic nucleus of potassium is composed of 19 protons and 20 neutrons.

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1. What particles compose the atomic nucleus?

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2. Calculate the number of protons and neutrons composing the nuclei of the atoms of (a) fluorine and (b) radium. Round the mass of the atoms to a whole number.

7.5 Isotopes

We know that atoms can be divided and that they do not last forever. Now we have to decide if the atoms of one and the same element are identical in all respects. For example, do they have the same weight?

Since the mass of electrons in the atom is insignificant compared with the mass of the nucleus, the mass of the atoms of elements should be a multiple of the proton or neutron mass, i.e. approximately a multiple of unity. In other words, masses of atoms should be expressed by whole numbers (to be more accurate, close to whole numbers). This conclusion holds for some elements. But there are many other elements whose relative atomic weights are expressed by fractional numbers. For example, the atomic weight of chlorine is given as 35.45. But actually there is no single chlorine atom in nature that weighs 35.45 amu. The element chlorine is a mixture of two types of atoms; some of them have the weight of 35 amu and others 37 amu. The found relative atomic weight of chlorine 35.45 is only a mean value of the weights of chlorine atoms which is determined with due consideration of the proportions in which the lighter and heavier chlorine atoms are found. Chlorine contains a greater proportion of lighter atoms and the mean atomic weight is therefore 35.45.

Like chlorine, most chemical elements are mixtures of atoms with different weights but having the same charge of their nuclei. The atoms of one and the same element differing in weight are called *isotopes* (from Greek *isos* equal and *topos* place).

A natural mixture of the two isotopes of chlorine atoms is designated by the chemical symbol Cl. But when we speak about one isotope separately, we have to superscribe the rounded atomic weight of the isotope in question: ${}^{35}Cl$, ${}^{37}Cl$.

Like chlorine, most chemical elements are mixtures of isotopes. Nuclei of isotopes of each element contain one and the same number of protons but the number of neutrons in them is different. For example, the nuclei of the isotopes ${}^{35}Cl$ and ${}^{37}Cl$ contain 17 protons (the atomic number of chlorine is 17) and different number of neutrons: the nuclei of ${}^{35}Cl$ contain 18 neutrons while that of ${}^{37}Cl$ have 20 neutrons.

If one element predominantly contains its heavier isotopes while the element that comes next to it in the periodic system is mostly composed of its lighter isotopes, the situation may arise where the atomic weight of the element with a higher atomic number will be smaller than that of the element with a lower atomic number. This is exactly the case with argon and potassium.

The extraordinary similarity of chemical properties of isotopes of one element (despite their different weight) proves the correctness of the earlier conclusion: *the properties of chemical elements depend mostly on the charge of their atomic nuclei rather than on their atomic weights.*

The information available on isotopes makes it possible to give a more accurate difinition of a chemical element. *A chemical element is a type of atoms with a similar charge of its nucleus.*

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1. What is: (a) an isotope, and (b) a chemical element from the standpoint of the theory of atomic structure?

2. What special property of isotopes accounts for the name 'isotope'?

3. Argon consists of three isotopes, viz. ${}^{36}Ar$, ${}^{38}Ar$, and ${}^{40}Ar$. Potassium also has three isotopes: ${}^{39}K$, ${}^{40}K$, and ${}^{41}K$. The lightest isotope of potassium makes up 93 per cent of the element while argon's heaviest isotope makes up 99 per cent. Which has the greater atomic weight, argon or potassium?

4. Natural hydrogen consists of ${}^{1}H$ and ${}^{2}H$ isotopes, and oxygen consists of ${}^{16}O$ and ${}^{17}O$. Natural water consists of various molecules: ${}^{1}H^{2}H^{16}O$, ${}^{1}H_2^{16}O$, etc. Give formulas for other varieties of water molecules and calculate their molecular weights. What molecules prevail in natural water? What water molecules are the least abundant? Explain your answer.

7.6 Structure of the Electron Shells

We must now understand why the properties of chemical elements change periodically with the increasing charge of the atomic nucleus. It is not enough to know the composition of the atoms of chemical elements. Take, for example, sodium (atomic number 11) and neon (at. No. 10). Their chemical properties are quite dissimilar: neon is an inert gas while sodium is one of the most active metals. At the same time the difference in the structure of their atoms is quite insignificant: the charge of the sodium nucleus is only one unit higher than that of the neon nucleus, and it has only one electron more than neon. In order to understand why such insignificant differences in the structure of the atoms of sodium and neon can bring about such marked differences in the properties of these elements, it is necessary to get acquainted with the structure of their electron shells.

The nucleus as we know is in the centre of the atom of each element, whereas the electrons that form the electron shell of an atom are found at different distances from the nucleus, thus forming layers: one electron layer may be nearer and others farther from the nucleus. The electrons that are closer to the nucleus are more strongly attracted by it, and the force of attraction between more remote electrons and the nucleus is weaker. A plate II on page 228 shows the structure of atoms of the first 18 chemical elements. The diagrams show how many electron layers there are in the atom of each element (the layers are shown in the form of arches) and how many electrons are contained in each layer (their numbers are written inside the arches).

A hydrogen atom (No. 1) has the simplest structure: one electron rotates round the nucleus with the charge of +1. The nucleus of helium (No. 2) has the charge of +2 and two electrons are found to move round it. Both electrons of the helium atom are found at an equal distance from the nucleus and are equally attracted to it. (Remember that helium is an inert gas.) Hydrogen and helium form the first period; as distinct from all other periods, it only contains two elements. As distinct from other periods, it does not begin with an alkali metal.

The second period begins with the alkali metal lithium. The lithium atom (No. 3) has the same group of two electrons in the close vicinity of the nucleus (as in the helium atom), but there is a third (distinguishing) electron which is found farther from the nucleus (than the former two) and its attraction to the nucleus is weaker. The lithium atom has two electron layers, viz. an inner and an outer one, the former containing two electrons and the latter one. In the transition from lithium to beryllium (No. 4), transition from beryllium to boron (No. 5) etc., the charge of the nucleus increases by one unit, while one distinguishing electron is added each time to the electrons in the outer layer, until a full octet of eight electrons is found in the outer layer of neon (No. 10), the noble gas which completes the second period.

We shall further distinguish between atoms with complete and incomplete outer electron layers. *If the outer layer contains the maximum possible number of electrons it is considered complete and if this number is smaller, the layer is incomplete.*

The element that comes after neon is the alkali metal sodium (No. 11). It has the same two layers (one containing two electrons and the other eight electrons), as in the neon atom, but there is also an eleventh electron which is still more remoted from the nucleus. A third layer thus appears in sodium, which begins the third period in the periodic table. The number of electrons in the outer (third) layer increases by one with each new element in this period until the full number of eight is attained. This again occurs in an inert gas. This time the noble gas is argon.

Let us summarize. As the charge of the nucleus of the atom increases with the atomic number of the element, the structure of the electron shell of the preceding element is preserved and one distinguishing electron only is added. This electron is either added to the outer layer or it may begin a new layer. The first layer, which is the nearest to the nucleus, can hold only two electrons and its occupancy is exhausted in helium, the inert element which completes the first period. The second and third layers can be occupied by eight electrons as in neon and argon, the inert elements that complete the second and the third periods.

As electrons are accumulated in the outer layer, the properties of the elements change gradually through the period. The addition of a new electron layer accounts for the marked change in the properties of the elements: a new electron layer begins a new period.

One can now easily understand why the properties of chemical elements change periodically (regularly). Let us took again at colour plate I. Look at the outer electron layer of the atoms: the number of electrons in it recurs periodically with an increasing charge of the nucleus. The outer layer of the sodium atom has the same number of electrons as the outer layer of the lithium atom: only one electron.

The number of electrons in the outer layer of magnesium is the same as that in the outer layer of beryllium: two electrons, etc. Atoms of the elements belonging to one family thus have the same number of electrons in their outer layers, for example, the alkali metals have only one electron in their outer layers and the halogens have seven electrons.

Properties of chemical elements change periodically with their increasing atomic number because the number of electrons in the outer layer of the atoms also change regularly.

What is an electron? What is the state of an electron in the atom? The great contribution to the development of the theory of electron structure of the atom has been made by physicists. Using the periodic law they established the electron structure of atoms of elements to open the way to explanation of their chemical properties.

The state of an electron in the atom can be characterized graphically. Each electron in the atom moves round the nucleus. The velocity of the electron is so high that it is impossible to state that the electron may be

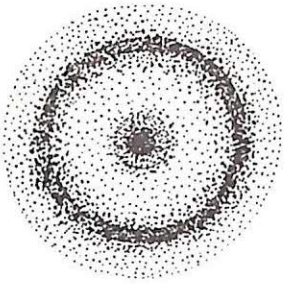

Fig. 7.3 Electron cloud of a hydrogen atom

found at any given point at a given time. The rapidly moving electron occupies a certain space round the nucleus and forms a kind of a cloud. The density of such an electron cloud is nonuniform and changes with the distance from the nucleus. It increases at points where the probability of finding an electron increases. If we speak about the region of maximum probability of finding an electron cloud, we can also speak about the shape of the cloud and its dimensions.

The one and only electron of the hydrogen atom moves about the nucleus to form a spherical cloud (Fig. 7.3). The maximum density of this cloud (the highest probability of finding the electron) is at a distance of 0.53×10^{-8} cm from the nucleus. The electrons that form spherical clouds, like the electron of hydrogen, are called *s* electrons. Clouds of *s* electrons differ in diameters depending on the layer in which the electron is contained. The closer to the nucleus an electron is found, the smaller the diameter of its cloud.

Electrons in atoms form clouds of other shapes as well. One of these resembles a dumb-bell. Electrons forming dumb-bell clouds are called *p* electrons. Each *p* electron moves round the nucleus so that it is alternately found on either side of the nucleus. These electrons differ not only in size (like *s* electrons) but also in their position in space: if the axes of the clouds formed by *p* electrons do not coincide, they are perpendicular to one another.

When the configurations, dimensions, and position in space of the clouds formed by two electrons are the same, both clouds join into one two-electron cloud. The electrons forming such two-electron clouds are called *paired* electrons. Each atom can contain maximum two electrons whose clouds are of the same configuration, size, and position in space. Electron clouds can thus join only in pairs. In the atom of helium, which comes next to hydrogen, the clouds of both *s* electrons are joined in one spherical two-electron cloud. The same two-electron cloud is contained in the form of the inner layer in the atoms of all other elements that follow helium.

Consider now Fig. 7.4 showing the structure of the outer electron layer for the atoms of the elements that belong to the second period. The inner layers are shown here by black circles (only for lithium and beryllium). The outer layer of the lithium atom has only one *s* electron whose cloud is spherical but the size exceeds greatly the size of the inner electron cloud. In the beryllium atom the second *s* electron of the outer layer forms a cloud of the

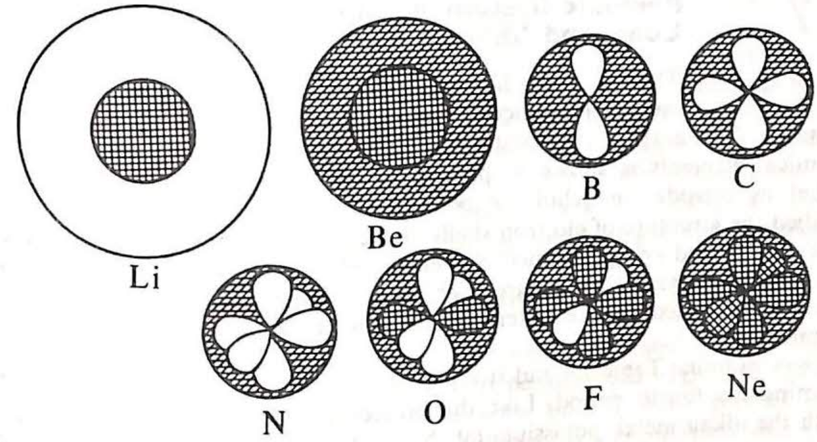

Fig. 7.4 Structure of outer electron layers in atoms of the elements of period II

same configuration which joins with the cloud of the first electron, like in the atom of helium. Two-electron clouds are shaded in the figure.

Beginning with boron, *p* electrons appear in the electron shells of atoms. A boron atom has one *p* electron, and a carbon atom has two *p* electrons. Their clouds are of the same size but they do not join together because their axes do not coincide. They form perpendicular one-electron dumb-bells. The next *p* electron, that appears in nitrogen, forms another dumb-bell whose axis is perpendicular to the former two axes. Three mutually perpendicular dumb-bells are thus formed.

The cloud of the sixth electron in the oxygen atom joins with the cloud of one of the preceding *p* electrons to form a two-electron cloud, while the other two *p* electrons remain unpaired, and an angle of 90° is left between them. The next *p* electron in the fluorine atom pairs with one of the unpaired electrons. And one electron still remains unpaired. Finally, all *p* electrons (like *s* electrons) become paired in neon.

The order of occupation of the outer layer of atoms by electrons is the same in all subsequent periods: the alkali metals have one unpaired *s* electron in their outer layers. The structure of the outer layers in all other noble gases is the same as in neon: they comprise two *s* electrons and six *p* electrons. All electrons in the outer layers of the atoms of inert gases are paired.

It follows that the structure of outer electron layers in atoms of elements changes periodically with increasing atomic number.

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1. Explain the periodic law from the standpoint of the theory of atomic structure.
2. Without consulting the colour plate I, draw the electron structure of the atoms of (a) carbon (No. 6), (b) phosphorus (No. 15), and (c) argon (No. 18).

7.7 Periodic System of Chemical Elements. Long and Short Periods

The periodic law underlies the natural classification of chemical elements, i.e. the periodic system of chemical elements. The graphic representation of this system in the periodic table of chemical elements is shown in plate I on page 226.

Let us consider in detail the periods of the periodic system. We have studied the structure of electron shells of the atoms in the first three periods. The first period comprises two elements, and the second and third periods, each eight elements. These are *short periods*, in which one distinguishing electron is added to the outer layer of the atom with increasing atomic number.

Now examine Table 7.6 and study the structure of electron shells of atoms forming the fourth period. Like the preceding short periods it also begins with the alkali metal, potassium (at. No. 19). A new layer with one electron appears in potassium. Another electron is added in calcium which comes next (at. No. 20). If distinguishing electrons were further added to the outer layer, the period would end with a halogen and an inert element. But the eighth box in the fourth period is occupied by iron. This very well known element is also preceded by metals.

Beginning with the third element, scandium (at. No. 21), the adding of electrons to the outer layer is suspended and the distinguishing electrons are now added to the eight electrons in the penultimate layer until their number

Table 7.6

Structure of Atoms of the Elements in the 4th Period

At. No.	Element		Distribution of electrons in layers			
			I	II	III	IV
19	*Potassium*	K	2	8	8	1
20	*Calcium*	Ca	2	8	8	2
21	*Scandium*	Sc	2	8	8 + 1	2
22	*Titanium*	Ti	2	8	8 + 2	2
23	*Vanadium*	V	2	8	8 + 3	2
24	*Chromium*	Cr	2	8	8 + 5	1
25	*Manganese*	Mn	2	8	8 + 5	2
26	*Iron*	Fe	2	8	8 + 6	2
27	*Cobalt*	Co	2	8	8 + 7	2
28	*Nickel*	Ni	2	8	8 + 8	2
29	*Copper*	Cu	2	8	18	1
30	*Zinc*	Zn	2	8	18	2
	...	...	...	...	...	...
34	Selenium	Se	2	8	18	6
35	Bromine	Br	2	8	18	7
36	Krypton	Kr	2	8	18	8

Italicized are the metals.
The symbols of the elements of the secondary subgroup are enclosed in a frame.

reaches 18. During this occupation of the penultimate layer the number of electrons in the outer layer remains two (see Table 7.6).

But there are exceptions. In the transition from nickel (at. No. 28) to copper (at. No. 29) one of the outer electrons moves to the penultimate layer together with the last electron added. Thus one electron only remains in the outer layer of the copper atom while the penultimate layer now has the full set of 18. In the elements that come after copper the same complete penultimate layer is found, and the outer layer is now filled again until the number of electrons in them is eight in krypton, the inert gas that completes the period (at. No. 36).

Since the fourth period, unlike the short periods, includes the elements in which the penultimate layer is completed to 18 electrons, the number of elements in the group increases to 18. The periods containing more than eight elements are called *long*. Long and short periods both begin with alkali metals and both end with the inert elements. But in short periods the transition from the alkali metal to the inert element is accomplished after six, and in long periods after a greater number of elements.

△ Draw electron diagrams of atoms of the elements with atomic numbers 33 and 37.

The elements in the periodic table are arranged in periods and groups. The periods are designated by the Roman numerals. The first period consists of two elements, viz. hydrogen and helium. The second and the third periods comprise eight elements each, the fourth and the fifth periods have 18 elements each, and the sixth period, 32 elements. At the present time the seventh period comprises 18 elements but it is not complete and the search for the missing elements is being continued.

Each long period is subdivided into two families or series in which the higher valency of the elements in their oxides increases from 1 to 7. These series are connected by three metals with similar properties which however have no analogues in short periods. These elements of the long periods are given in colour while the others are all arranged one beneath the other in short periods. With this arrangement, each element of the long period is placed in one vertical column together with the elements of short periods which have the same higher valency. For example, the fifth period which begins with rubidium and ends with xenon is divided into two series. The upper series ends with three metals, viz. ruthenium, rhodium and palladium, while the lower series begins with silver. The higher valency of the elements in their oxides in both long and the short periods increases from 1 in rubidium and silver to 8 in ruthenium and xenon.

The upper series of each long period is given an even number and the lower an odd number. Even series only contain metals, and nonmetals appear at the end of odd series (i. e. at the end of the period); their chemical symbols are given in red colour.

The structure of the elements in the even and odd series of long periods is different. Only the two first elements in an even series have eight electrons in the penultimate layer, whereas in the elements which follow them (up to the end of the even series) distinguishing electrons are added to the penultimate layer. These elements are given in yellow areas. The atoms of the elements standing in odd series have completed penultimate layers (18 electrons) and *distinguishing* electrons are now added to the outer layer, as in elements of periods II and III, where their number increases from 1 to 8.

We have thus discussed the changes in the properties of chemical elements in the periods. Let us now consider variation of their properties in the columns of the periodic table.

7.8 Groups and Subgroups of the Periodic Table

Elements united in one vertical column of the periodic table make up a group of elements.

The periodic table comprises eight groups of elements marked by the Roman numerals. The eighth group consists of elements that connect the even and odd series, and the inert gases. The number of the group coincides numerically with the higher valency of these elements in compounds with oxygen. There are only a few exceptions. For example, copper, an element in the first group, may also exhibit a valency of 2, while fluorine, an element in the seventh group, does not form compounds in which its valency is 7. Only few elements of the eighth group (e.g. osmium and xenon) have a valency 8 in their higher oxides.

Hydrogen is put in one group together with the alkali metals because its valency in the oxide (water) is 1.

In addition to a tervalent element lanthanum La (at. No. 57), that stands between a divalent metal barium Ba (at. No. 56) and a tetravalent metal hafnium Hf (at. No. 72) the sixth period also includes some other 14 metals whose properties are very much like those of lanthanum. These form the family of lanthanides. Since the lanthanides are similar to lanthanum in their atomic structure and are usually tervalent, only one box is given to the entire family in the periodic table (between barium and hafnium), whereas their complete list (arranged in the order of their increasing atomic numbers) is given separately at the bottom of the table. The actinides, the elements following actinium Ac, are also given separately.

The similarity between the lanthanides and actinides depends on the fact that the electrons in them are added to the third layer (as one moves towards the nucleus), while the number of electrons in the two outer layers remains the same.

Each group is divided into two subgroups. The chemical symbols of the elements of one subgroup are written in the right part of their boxes in the table, and the elements of the other subgroup in the left side of their boxes. For example, group VII includes the subgroup of the halogens and of manganese (Mn, Tc, Re).

Subgroups comprising the elements of long and short periods are called the main subgroups, while those comprising only the elements of long periods, are called secondary subgroups.

The subgroup of the halogens, for example, is the main subgroup and the subgroup of manganese is the secondary of the seventh group.

In what subgroups, main or secondary, do the known nonmetals sulphur, oxygen, nitrogen, carbon, the inert gases, and the halogens stand? They all belong to the main subgroups of groups IV, V, VI, VII and VIII. The secondary subgroups contain metals alone.

Below each group one can find the general formula of higher oxides of the elements belonging to this group and their volatile compounds with hydrogen. The general formula of the oxides refers to all elements belonging to this group (irrespective of the subgroup to which they may belong). But the volatile hydrides may be formed by nonmetals alone. The formulas of the hydrides are therefore written under the symbols of the elements of the main subgroups.

In the elements of the main subgroup the metallic character increases and nonmetallic properties decrease with their increasing atomic numbers. For example, the metallic properties of the alkali metals increase with their increasing atomic number, while nonmetallic properties in the halogens decrease.

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1. What elements have (a) 8, and (b) 18 electrons in their penultimate layer?
2. What number of electrons are there in the outer, and penultimate layers of the atoms of (a) silver (at. No. 47), (b) gold (at. No. 79), (c) radium (at. No. 88), (d) zinc (at. No. 30), (e) mercury (at. No. 80), (f) lead (at. No. 82), (g) tin (at. No. 50), (h) tellurium (at. No. 52), (i) tungsten (at. No. 74), (j) tantalum (at. No. 73), (k) rhenium (at. No. 75) and (l) zirconium (at. No. 40)? In some cases the answer can only be presumed. Explain why.
3. What is: (a) a period, (b) a group, and (c) a subgroup of the periodic table?
4. How can it be explained that boron and aluminium belong to the main subgroup of group III but boron is a nonmetal while aluminium is a metal?
5. By what distinguishing traits are the elements placed in (a) groups and (b) subgroups?
6. Write formulas of hydroxides of magnesium, zinc, and calcium. Which of them is the strongest and which is the weakest base? Explain your answer.
7*. The density with respect to hydrogen of a higher oxide is about 22. What is the atomic weight of this element? Reason your answer (using the periodic law). Name the element and characterize its position in the periodic table. Prove that your solution of the problem is correct and is the only possible one.

7.9 Characterizing the Element by Its Position in the Periodic Table and Atomic Structure

The position of an element in the periodic table gives much information about its properties. Consider calcium, for example. Its atomic number is 20 and it stands in the fourth long period, in the main subgroup of group II, in the fourth (even-numbered) series. Since even series of long periods only contain metals one can conclude that calcium is a metal. This is an element of the second group and the formula of its oxide is CaO; it does not form volatile compounds with hydrogen. The properties of calcium should resemble those of magnesium, the element above it but they must be of a more pronounced metallic character. What information concerning the atomic structure of calcium can be derived from its position in the periodic table?

Its atomic number is 20 which means that the charge of the nucleus of the calcium atom is +20 and its electron shell contains 20 electrons. *The number of electron layers in an atom coincides with the number of the period to which it belongs.* It follows therefore that the calcium atom has four electron layers (it belongs to the fourth period). *The number of electrons contained in the outer electron layer of main group elements is equal to the number of the group.* This does not hold, however, for the elements of secondary subgroups (the yellow area) because in them it is the penultimate layer which is being filled. Calcium stands in the main subgroup of group II; hence its outer layer contains two electrons.

The outer layer is completed in the atoms of the inert elements. In the atoms of helium this layer contains only two electrons while in the atoms of all other inert gases the outer layer contains the full octet. Except in the inert elements, the outer layer of atoms of all other elements is incompletely occupied by electrons.

The inert elements thus differ in their structure from all other elements.

Continue comparing the electron structure of elements. Examine Table 7.6 and the periodic table (plate I on page 226). If we examine the electron diagram of an unknown element we can decide at first glance if this element is a metal or a nonmetal. Consider the outer layer: the number of electrons in the outer layer of metals usually contains one or two electrons while the outer layers of nonmetals are close to completion. Hydrogen and helium might appear as exceptions but although the outer (and only) layer of helium contains only two electrons, the layer is complete. The outer (and only) layer of hydrogen contains a single electron but only one electron is missing to complete the layer.

The atoms of metals thus differ from those of nonmetals in their structure (small number of electrons in the outer layer) and in their properties (weak attraction of the electron to the nucleus). Why are electrons in the outer layers of metal atoms weakly attracted? The outer electrons are held in the atom by the attractive force of the nucleus and the electrons of the inner layers that surround it. The summary charge of the nucleus and the inner electrons is positive and is numerically equal to the number of outer electrons: this summary charge of the elements of the first group is thus +1, of the elements of the second group +2, of the third group (the main subgroup) +3, etc. You know from your physics course that oppositely charged bodies are attracted to one another, and the force of attraction increases with a decrease in distance between the bodies. As the outer electron layer nears completion, the summary charge of all elements increases and the bond between the outer electrons and the nucleus therefore strengthens too.

So as the atomic number increases in each period, metallic properties of the elements first weaken and then change to nonmetallic properties.

How do the properties of the elements in the main subgroups change? The summary charge of the elements standing in the main subgroups (for example, in Li, Na, K, Rb, Cs or F, Cl, Br, I) remains unchanged but the number of electron layers grows and the radius of the atom increases accordingly. The distance from the nucleus of the atom to the electrons in the outer layers increases and the force of attraction between them weakens. Therefore, the greater the atomic number of an element, the easier its atom loses its outer electrons: the metallic character of the elements in the main subgroups increases with the atomic number. We have observed this phenomenon in the subgroup of the alkali metals.

The weaker the atom holds its own electrons, the more difficult it gains additional electrons: the nonmetallic character of elements weakens with the increasing atomic number of the elements in the main subgroups. We have observed this phenomenon in the halogens. In metals the outer electrons are bonded more weakly while in the atoms of nonmetals more strongly. This accounts for the different physical properties of metals and nonmetals in the free state. The attraction of electrons in the outer layer of metal atoms is so weak that the electrons may leave their atoms and move freely between them. These wandering electrons account for electric conductivity (and also for other physical properties) of metals. Typical nonmetals have all their electrons strongly attracted to the nuclei, free electrons are absent, and electric conductivity is therefore absent as well.

We shall further find out that not only general physical but also general chemical properties of metals and nonmetals depend on the same factor, namely, the strength of attraction of the outer electrons to the nuclei of atoms.

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1. The atoms of which elements have their outer layers fully occupied by the electrons? How many electrons do these outer layers contain?
2. How many electrons should be added to the outer electron layers of hydrogen, oxygen, sulphur, and nitrogen atoms to complete them?
3. What is the number of electron layers and electrons in the outer layer of the atoms of elements which have the following atomic numbers: 55, 53, 84, 88, 33, 36? Name each of these elements.
4. Describe the properties of manganese, nitrogen, phosphorus and radon by their position in the periodic table. Specify the following: number of the period; number of the group; main or secondary subgroup; metal or nonmetal; formula of a higher oxide; formula of a volatile hydride, if any; charge of the nucleus, and the number of electrons; the number of electron layers in the atom shell; the number of electrons in the outer layer; whether or not the outer layer is completed.
5. Determine the number of group and series (even or odd) of a given element, and decide if it is a metal or a nonmetal from the following of its properties: (a) the outer layer contains 6 electrons and the penultimate layer contains 18 electrons; (b) the outer layer contains 4 electrons and the penultimate 18 electrons; (c) the outer layer contains 2 and the penultimate 14 electrons; (d) the outer layer contains 1 and the penultimate 16 electrons.

1. Using your cards (Fig. 7.2) make up the second period of the periodic table. Replace the card of beryllium with the other card where the atomic weight is incorrectly written (13.5 as it was thought to be before Mendeleev) and the valency of beryllium is not given correctly either (3). Show what discrepancies in the periodic law might occur from such a substitution.
2. Put aside any card you may choose and try to make up the second and the third periods from the remaining cards placing them one beneath the other as before. Show the discrepancies in the periodic law that might occur from such a rearrangement. How can the proper place for a missing element be found without referring to the atomic numbers of the elements in the cards?

7.10

Transmutations of Chemical Elements

It follows from the definition 'chemical element' theat any chemical element keeps its identity while the charge of its nucleus remains unchanged. Hence if we can change the charge of the atomic nucleus of an element we can convert it into another element.

Atoms do not remain unchanged for ever. The elements with high atomic numbers are destroyed spontaneously and turn into other elements. Particles that are emitted by the nucleus of an atom can in turn induce transmutations of some chemical elements into others. These transmutations are called nuclear reactions. They are the subject matter of physics.

Some elements can be transformed into others by streams of fast particles emitted by nuclei of atoms during their radioactive decay. But these streams of particles, that will destroy or otherwise change the atomic nuclei of other atoms, can also be produced artificially. Thus man learnt how to perform hundreds of such conversions and to produce atoms that have not been found in nature. Man-made isotopes of carbon, oxygen, phosphorus and other elements have been obtained. They differ from the corresponding naturally occurring isotopes in their atomic weights and stronger radioactivity. Because of the latter property they have not survived in nature. Man has also artificially produced new chemical elements whose atomic numbers are greater than that of uranium, the element which formerly occupied the last box in the periodic table.

Thus the element with the atomic number of 101, mendelevium Md, has itself been prepared from another man-made element with the atomic number 99, einsteinium Es; the latter was bombarded with the nuclei of helium atoms which have been accelerated to tremendous velocities so that the mutual repulsion of the nuclei might be overcome. As the helium nuclei with their charge of + 2 met with the nuclei of the element No. 99, they fused with them to produce new nuclei with the charge 99 + + 2 = 101. The new nuclei attracted the missing electrons to turn into neutral atoms of a new element

$${}_{99}\mathrm{Es} + {}_{2}\mathrm{He} = {}_{101}\mathrm{Md}$$

(the charges of the atoms are subscribed on the left side of the chemical symbol). The periodic law is a kind of instruction manual on how to create artificial elements, just as it served as a guide in the search for new natural elements that had not been discovered before Mendeleev formulated his law. The Americans, who created the new element No. 101, gave it the name of mendelevium in the honour of the great Russian scientist Dmitry Mendeleev who worked out the system by which the properties of elements, not yet discovered, can nevertheless be predicted.

One of the methods for producing elements that do not occur in nature is to place substances in a nuclear reactor where neutrons are continually emitted. Nuclei of stable natural isotopes capture neutrons to increase their atomic weights by 1 amu and convert into radioactive isotopes of the same element, for example,

$$^{58}_{26}\mathrm{Fe} + ^{1}_{0}n = ^{59}_{26}\mathrm{Fe}$$

(the letter n stands for neutron).

Radioactive isotopes have the same chemical properties as the parent elements: they enter the same reactions and are involved in the same physiological processes. An artificial radioactive isotope of carbon, for example, is involved in the process of assimilation of natural carbon by plants. These artificial isotopes can easily be identified in compounds by special instruments sensitive to radioactivity. Radioactive isotopes can thus be used as tracers. For example, a negligible amount of radioactive carbon(IV) oxide may be added to carbon dioxide which is used to feed plants. Organic compounds formed in the plant are then isolated from it at various time intervals. By establishing which of these compounds have become radioactive (i.e. include the tracer, radioactive carbon) and by determining the time intervals during which these organic compounds have turned radioactive, the researchers can draw conclusions: through which intermediate compounds, and in what sequence carbon passes in the plant before it becomes a component of starch.

7.11 Importance of the Periodic Law

The role of any scientifically grounded theory is not only to explain the known facts but also (and more importantly) to enable new information to be predicted.

When Mendeleev worked developing the periodic law he had only 63 elements at his disposal and the atomic weights of many of them were incorrectly determined. For example, the atomic weight of beryllium was considered to be 13.5 instead of 9; moreover, beryllium was considered to be a tervalent metal. If the atomic weight of 13.5 were correct, beryllium should come between carbon (at. wt. 12) and nitrogen (at. wt. 14). The regular character of changes in the properties of elements would then be broken because the metal beryllium would be placed between two nonmetals, carbon and nitrogen, and a tervalent boron would then come after a univalent element, lithium. From these considerations Mendeleev concluded that the atomic weight of beryllium should be intermediate between the atomic weights of lithium (7) and boron (11), i.e. about 9, while the valency of beryllium should be 2 rather than 3. Later studies showed that the atomic weight of beryllium is indeed 9 and its valency actually is 2.

Using the same method Mendeleev corrected atomic weights of some other elements which otherwise were 'out-of-place' in his periodic table.

When making out his periodic table Mendeleev left many empty boxes because the elements possessing the predictable weights and properties had then not yet been discovered. Mendeleev concluded that such elements must exist in nature but they were simply unknown to man. The properties of these hypothetical elements which, according to Mendeleev, should be intermediate between the properties of the four neighbouring elements, i.e. the elements that stand to the left and to the right of an unknown element in the period, and above and under this element in the subgroup. Thus Mendeleev gave a detailed description of the properties of three elements which were not known at that time. And he gave them the names of ekaboron, ekaaluminium and ekasilicon. Within 15 years after Mendeleev's prediction these three elements were discovered. In order to show the accuracy of Mendeleev's prediction consider Table 7.7 (it is not necessary to remember it by heart) which compares the properties of ekasilicon with the properties of germanium which was later discovered by other researchers.

Now that we have become acquainted with the theory of atomic structure it is easier to understand the great importance of the scientific achievement of Mendeleev who discovered the periodic law. This discovery opened a new era in the development of chemistry and related sciences such as physics, geochemistry, and space chemistry. Before the periodic law was formulated, the discovery of each new element, substance, or chemical reaction was unexpected and accidental. Since the discovery of the periodic law, the progress of chemistry has acquired the character of a science whose lines of development can be planned. The periodic system of chemical elements has become a compass, a guiding star for chemists in their further research. Armed with the periodic law they uncovered new chemical elements, created some elements that do not exist in nature and produced new compounds with the required and predicted properties.

Table 7.7

Properties of ekasilicon as predicted theoretically by Mendeleev	Properties of germanium, established experimentally
Atomic weight, 72	Atomic weight, 72.6
Grey high-melting metal	Grey high-melting metal
Density, relative to water, 5.5	Density, relative to water, 5.35
Obtained by reduction of its oxide with hydrogen	Obtained by reduction of its oxide with hydrogen
Formula of the oxide, EsO_2	Formula of the oxide, GeO_2
Oxide density relative to water, 4.7	Oxide density relative to water, 4.7
The chloride $EsCl_4$ should be liquid, density relative to water, 1.9; boiling point about 90°C	The chloride $GeCl_4$ is a liquid, density relative to water, 1.887; boiling point, 86 °C

One of the most rarely occurring elements rhenium (at. No. 75) would not have been discovered unless its existence and properties (up to the practical uses, the minerals in which it might be contained, and the methods by which it might be recovered from them) had been predicted from the periodic law system.

The entire universe, as far as the remotest stars from which light reaches us (after millions of years), consists of the same elements that compose the Earth. Neither the existence of any element, nor any property of each element are accidental. All elements are interconnected genetically and their relationships are disclosed to us by the periodic law.

The periodic law has opened the way to a study of the structure of atoms and their nuclei. The practical result of these studies has been the discovery of nuclear energy. Like other great discoveries that explained not only separate facts or groups of facts but the entire scope of the science, the discovery of the periodic law and periodic system of elements was highly valued by the outstanding thinkers of the world. Friedrich Engels considered Mendeleev's discovery a great scientific triumph.

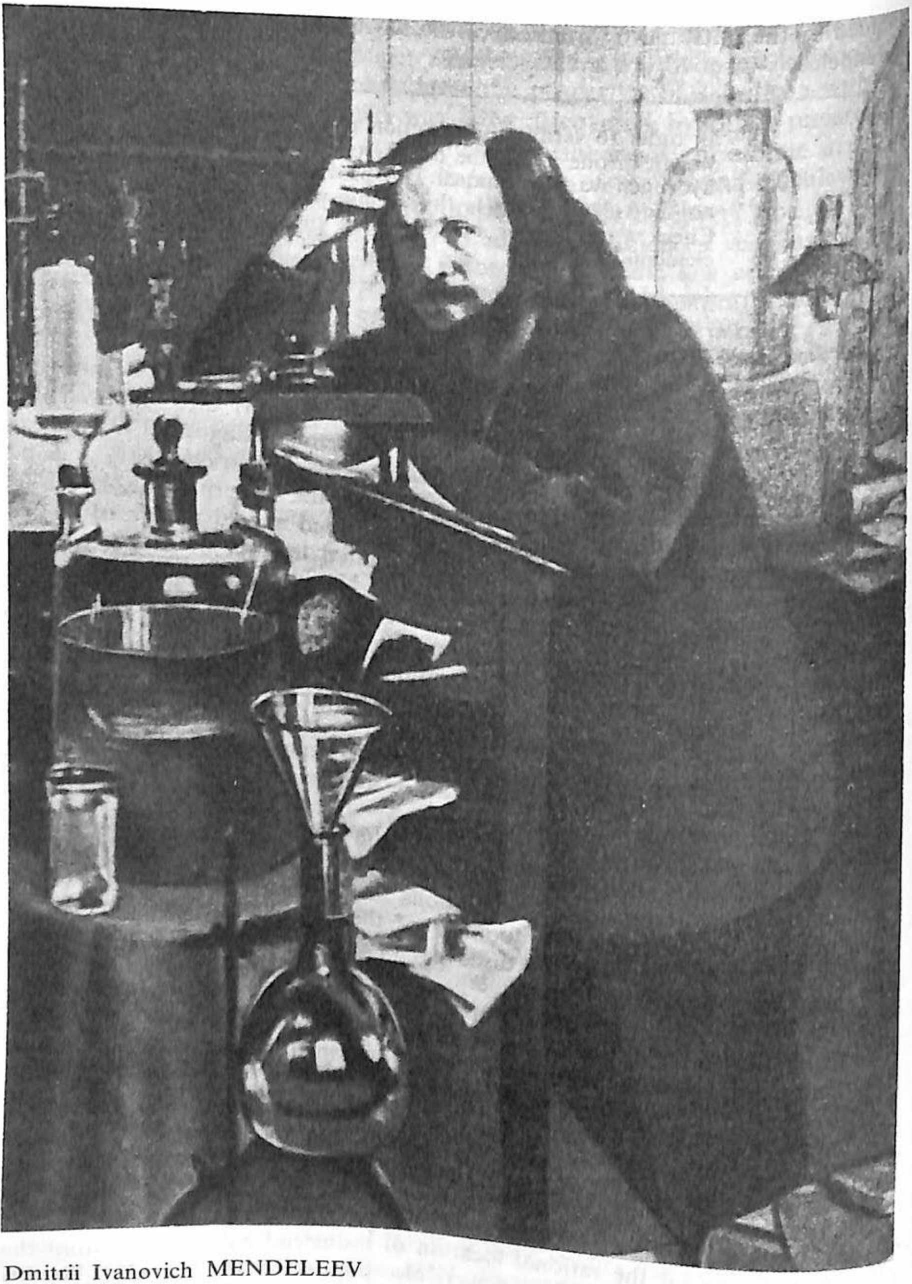
■ In order to verify the correction made by Mendeleev to the atomic weight of one metal, the density of vapour of its chloride relative to hydrogen was determined. This proved to be about 40. The metal is not univalent. What is the atomic weight of this metal? Name it. Check your answer by consulting the periodic table of chemical elements.

7.12 The Life and Work of Mendeleev

Dmitry Ivanovich Mendeleev was born in 1834 into the family of gymnasium (grammer school) director at Tobol (Siberia). After gymnasium he studied at the Central Pedagogical Institute in St. Petersburg (Leningrad) where he showed an interest in chemistry and did his first scientific research, and this determined the pattern of his later life. He graduated from the Institute and was awarded a gold medal. After two years of teaching in a school he was appointed lecturer at the Petersburg University. An important event in his life was his journey to Western Europe where he took part in the historical World Congress of chemists at Karlsruhe. Dalton had suggested an erroneous idea of how atomic weights of chemical elements might be determined. This created irreconcilable contradictions between chemists and some of them even denied the existence of atoms. The congress at Karlsruhe gathered to resolve these contradictions and disagreements. The opponents of the atomic theory were defeated: indisputable and self-evident methods for determining atomic weights of elements were worked out and adopted.

Soon Mendeleev undertook research in the field of solutions, namely, he studied the combination of alcohol with water. From then on Mendeleev worked to develop the theory of solutions that would explain dissolution by the formation of unstable compounds of the solute with the solvent. He became world famous after the discovery of the periodic law in 1869. True, he had already taken the first steps in this direction when he was still a student. The method of determination of atomic weights of chemical elements adopted at Karlsruhe gave Mendeleev the necessary material for his generalizations, although atomic weights of some elements still remained incorrect.

Theory and practice were usefully connected in all Mendeleev's research. The field of his interests was very wide. He made important contributions to the theory and practice of accurate measurements, and to a theory of aviation, physics, and chemical technology. Much effort was spent by Mendeleev in arguing for a rational utilization of Russia's natural wealth and on propaganda for the rational location of industrial enterprises within the country. His pedagogical activities were also important. He himself called his pedagogical work another service to the motherland. The final aim of science was regarded by Mendeleev as being scientific prediction and the practical



Dmitrii Ivanovich MENDELEEV
(1834–1907)

utilization of advances in science. He regarded a contribution to the well-being of his own motherland and to its economic and political independence as being the object of his own scientific work.

Being an ardent patriot, Mendeleev had many enemies among the officials of tsarist Russia and this prevented his election to the Academy in St. Petersburg, though he was an active member of academies of sciences of almost all other countries of the world.

During the student revolts of the 90s of the last century he took the part of the students for which he was rudely reprimanded and forced to retire from the university.

Mendeleev died in 1907. A huge crowd attended the funeral. The periodic table of chemical elements was carried in front of it. The scientific and technical ideas of Mendeleev have since been developed and put to practical use in many works of scientists in the Soviet Union and other countries.

8 Chemical Bond. Structure of Substance

8.1 Covalent Bond

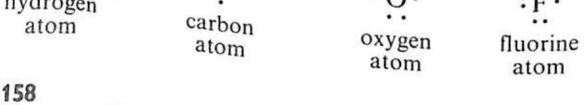
The planets of the solar system are held in their orbits by the forces described in the law of gravitation. The molecules in a drop of water are held together by the intermolecular forces. We now have to answer the question, what forces hold atoms in molecules and how chemical bonds arise between them. Consider first the structure of substances whose molecules consist of similar atoms.

It is necessary first to understand why, in contrast to all other elements, the inert elements hardly form chemical compounds. Also remember that neither do the atoms of the inert elements combine with one another: the molecules of the inert gases are therefore monatomic in contrast to diatomic molecules of all other nonmetals. We have already learnt that the atoms of the inert elements differ from the atoms of all other elements in that their outer electron layer is complete. This fact probably accounts for the chemical inertness of the inert elements and the monatomic character of their molecules. Conversely, the ability of atoms of all other elements to combine with one another depends on the incomplete occupation of their outer layers with electrons.

According to the electron theory, the complete (fully occupied) electron layers that are found in the atoms of the inert elements (two electrons in helium and eight electrons in all other inert elements) are especially stable electron configurations, which imparts chemical inertness to the atoms of the noble elements.

In order to better understand the essence of bonding between identical atoms (e.g. of oxygen, hydrogen, or chlorine into their diatomic molecules H_2, O_2, and Cl_2), let us first consider the formation of a hydrogen molecule. The hydrogen atom consists of a nucleus with the positive charge of + 1 and one negatively charged electron. When two hydrogen atoms meet, the nuclei of both attract the electron cloud of the other atom. The electron clouds thus overlap (Fig. 8.1) and the negative charge in the zone of overlapping becomes more condensed. This compensates for the mutual repulsion that arises between the two nuclei bearing the same charge. The electron of each separate hydrogen atom is now shared by the nuclei of both. The electron pair is said to be shared.

Let us designate the electrons in the outer layer by the corresponding number of dots as shown below:



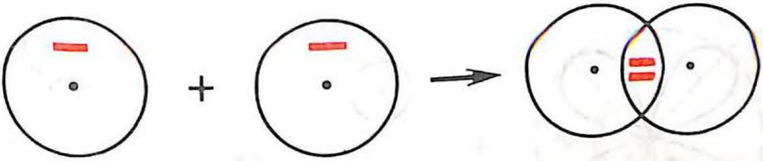


Fig. 8.1 Formation of a hydrogen molecule from hydrogen atoms

The formation of a hydrogen molecule from two hydrogen atoms may then be shown as:

$$H\cdot + \cdot H \rightarrow H:H$$

Two electrons, from each of the two hydrogen atoms, have formed an electron pair which is shown in our diagram by two dots placed between the symbols of the atoms.

The bonding of atoms by electron pairs is called covalent bonding.

When two identical atoms are bonded with one another, the shared pairs of electrons complete the outer layers of both atoms. Consider another example, the formation of a chlorine molecule. The outer layer of the chlorine atom contains 7 electrons. One of them is unpaired and it tends to join the unpaired electron of the other chlorine atom. Two electrons, from each of the two chlorine atoms, become shared, i.e. they perform a kind of double duty: they complete the octets in two chlorine atoms in the chlorine molecule. In other words, they form a covalent bond:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

Covalent bonding ensures completion of the outer electron layer which now becomes stable. But only six out of the eight electrons in the octet belong completely to one of the atoms while the remaining two electrons are shared between them. Both atoms in a molecule of nitrogen N_2 have three shared electron pairs $(:N\vdots\vdots N:)$. Each of the three electron pairs involves one electron from each of the two nitrogen atoms.

Covalent bonding, however, occurs not only between identical atoms but between different atoms as well. Hydrogen halide and water molecules also have covalent bonds. When a chlorine atom approaches the atom of hydrogen, the clouds of unpaired electrons overlap to form the area of increased density of the negative charge as happens in the case of formation of the hydrogen molecule H_2. One covalent bond is formed:

$$H\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \rightarrow H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

The oxygen atom has two unpaired electrons. When oxygen combines with two hydrogen atoms two covalent bonds are formed:

$$2H\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot}{O}}: \rightarrow H:\overset{\cdot\cdot}{\underset{\overset{\cdot\cdot}{H}}{O}}:$$

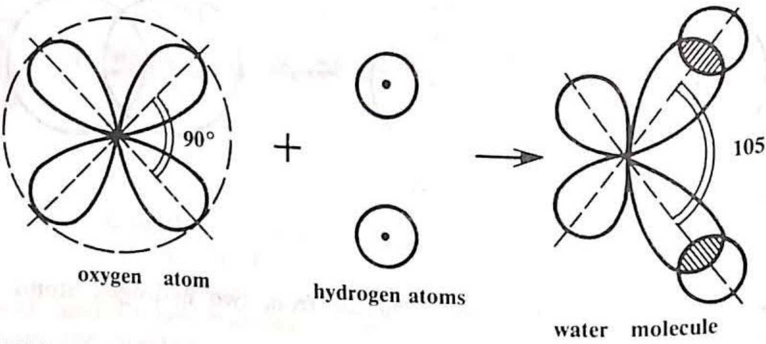


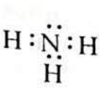
Fig. 8.2 Formation of a water molecule from atoms of hydrogen and oxygen. Clouds of unpaired electrons involved in the formation of chemical bonds are only shown

These bonds in the molecule of water are formed by pairing two unpaired *p* electrons of the oxygen atoms with unpaired electrons of the hydrogen atoms. The electron clouds formed by *p* electrons are elongated and their axes are mutually perpendicular. The angle of 90° between the covalent bonds remains almost unchanged. This is one of the reasons why the water molecule has an angular configuration (Fig. 8.2). The hydrogen atoms are attached to the oxygen atom at an angle of 105°, which is only slightly wider than the right angle (this is probably due to mutual repulsion of the hydrogen atom nuclei).

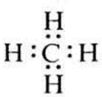
Each electron pair that connects two atoms may also be shown by a dash (instead of the dots). The dot formula then transforms into a structural formula, for example:

Electron-dot formulas

$\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$ $\quad$ $\mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:\mathrm{H}$



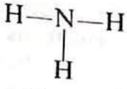
$$\begin{array}{ccc} & \cdot\cdot & \\ \mathrm{H}: & \mathrm{N} & :\mathrm{H} \\ & \cdot\cdot & \\ & \mathrm{H} & \end{array}$$



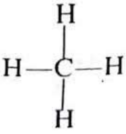
$$\begin{array}{ccc} & \mathrm{H} & \\ & \cdot\cdot & \\ \mathrm{H}: & \mathrm{C} & :\mathrm{H} \\ & \cdot\cdot & \\ & \mathrm{H} & \end{array}$$

Structural formulas

$\mathrm{H}{-}\mathrm{Cl}$ $\quad$ $\mathrm{H}{-}\mathrm{O}{-}\mathrm{H}$



$$\begin{array}{ccccc} \mathrm{H} & - & \mathrm{N} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

The electron-dot and structural formulas vividly show the sequence in which the atoms are arranged in a given molecule. The structural formula of water, for example, shows that the hydrogen atoms are connected with the oxygen atom but are not connected with each other.

?

1. Draw electron-dot and structural formulas of the following molecules: H_2, F_2, O_2, HF, N_2, H_2S.

△ 2. Unlike the molecules of all other nonmetals, the molecules of the noble gases are monatomic. Explain why.

8.2

Electronegativity

The character of chemical bonds depends on the nature of the atoms, i.e. on their structure and properties. The chemical bond accounts largely for the property of atoms known as *electronegativity*.

The ability of atoms to attract electrons that bond them with other atoms is called *electronegativity*. The stronger this electron-attracting power, the greater is electronegativity.

Let us see if it is possible to determine the electronegativity of an atom from its position in the periodic table. The more strongly the atom attracts its own outer electrons and those of other atoms, the greater is the electronegativity of a chemical element. We already know that removal of electrons from the atoms becomes more difficult and the capture of extraneous electrons becomes easier in periods with increasing atomic numbers of the elements. The same holds for the main subgroups with decreasing atomic number of the elements. This means that electronegativity of elements increases in the periods from left to right and in the main subgroups from bottom to top. Fluorine is therefore the most electronegative element. It occupies the upper right-hand corner of the periodic table (the inert gases are disregarded) and the position of any other nonmetal is either lower or to the left of fluorine, or both lower and to the left. This is why during reactions of fluorine with any other element (the noble gases with high atomic numbers included) the fluorine atoms attract the electrons of those elements.

Oxygen stands before fluorine (left of it) and in all its compounds, except with fluorine itself, it attracts the electrons of other atoms that combine with it.

The atoms of nonmetals (except fluorine) can both attract and repel electrons of other atoms depending on the particular element with which they are combining.

The elements below are arranged in the order of their increasing electronegativity

Si, As, H, P, Se, I, C, S, Br, Cl, N, O, F

When different chemical elements combine with one another the electrons are displaced from one element toward the other which stands to the right of this element in this series.

8.3

Polar and Nonpolar Bonds

In simple substances consisting of identical atoms a pair of electrons is equally shared since both atoms equally attract the electrons. This type of covalent bonding is called *nonpolar*. If however

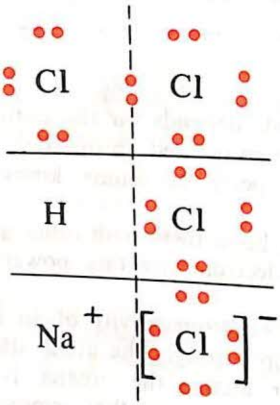


Fig. 8.3 Types of chemical bonds

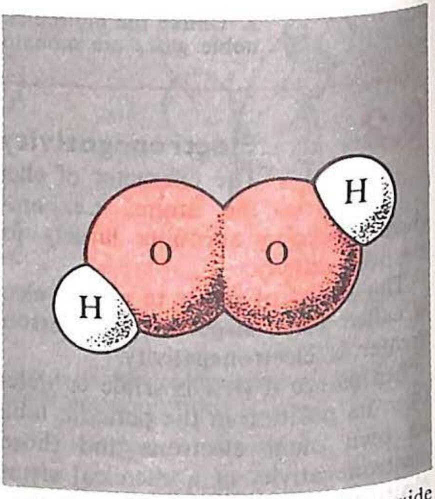


Fig. 8.4 Model of a hydrogen peroxide molecule

two different atoms share a pair of electrons the latter will be displaced toward the atom with a stronger electronegativity, i.e. toward the atom showing stronger attraction. A covalent bond of this type is called *polar*. Polar covalent bonds exist, for example, in the molecules of HF, HCl, H_2O. In the molecules of hydrogen halides and water the electron pairs are displaced from the hydrogen atoms toward the atoms of the halogen and oxygen.

Displacement of electron pairs from one atom toward another is sometimes shown graphically by placing the dots (designating the electron pair) closer to that element toward which the electron pair is displaced (Fig. 8.3).

? △

1. What two types of covalent bonds do you know?
2. What is the difference between polar and nonpolar covalent bonds and what is common to both types of covalent bonds?
3. Name substances in which only polar and only nonpolar covalent bonds exist.
4*. Look at Fig. 8.4 and draw an electron-dot and structural formulas of the molecule of hydrogen peroxide. Calculate the number of electrons contained in the outer layer of the oxygen atom, and the number of all chemical bonds in this molecule. Define the type of chemical bonds.

8.4

Ionic Bond

In order to understand better the character of chemical bonds in compounds of elements with pronounced differences in their electronegativities, compare the structure of atoms of the following three elements of the third period (see Table 8.1).

Table 8.1

Element	Nucleus charge	Distribution of electrons within layers			Chemical properties
		I	II	III	
Fluorine F	+9	2	7	–	Halogen. Combines with almost all elements. The most active nonmetal
Neon Ne	+10	2	8	–	Inert gas. Does not form chemical compounds
Sodium Na	+11	2	8	1	Alkali metal. Energetically combines only with nonmetals

The chemical properties of the elements change markedly with their increasing atomic number in the transition from F to Ne and from Ne to Na. In the former case this is probably due to completion of the outer electron layer (in Ne) and in the latter, due to the appearance of a new layer (in Na). When the outer layer becomes completed the chemical activity is lost, and when a new layer is begun chemical activity is restored but its character changes: fluorine most energetically combines with metals while sodium, with nonmetals.

The outer layer in the atoms of typical nonmetals (halogens, nonmetals of the main subgroup of the 6th group) is incomplete but nears completion: only one electron is missing to complete the full octet in the halogens, and only two electrons are needed to complete the outer layers in the elements of the oxygen subgroup. The atoms of these elements can therefore capture electrons from other atoms to complete their own outer layers.

Table 8.2 gives electron configurations of the atoms of chlorine and its nearest element, the inert gas argon. Only one electron is required to be added to the outer layer of chlorine in order to complete it. Suppose the chlorine atom captures the missing electron from outside. Into what will the chlorine atom change? Its electron shell contains now the same number of

Table 8.2

Particle	Nucleus charge	Distribution of electrons in layers		
		I	II	III
Chlorine atom Cl	+17	2	8	7
Chloride ion Cl^-	+17	2	8	8
Argon atom Ar	+18	2	8	8
Sodium ion Na^+	+11	2	8	0

8.4 Ionic Bond

electrons as is contained in the electron shell of argon; but the chlorine atom will not turn into the atom of argon because the charge of the nucleus remains + 17 whereas in argon it is + 18. Before the chlorine atom captures a new electron it remains neutral, i.e. uncharged, because the 17 units of the positively charged nucleus are counterbalanced by the 17 negatively charged electrons. When the chlorine atom captures one electron it turns into a negatively charged particle known as the chloride *ion*.

The outer layer is far from completion in typical metals: the outer layers of the alkali metals have only one electron and metals of the second group two electrons. The outer electrons of metals are easy to remove from their atoms and metals thus convert into positively charged particles in which the positive charge of the nucleus is not counterbalanced by the remaining electrons.

An electrically neutral atom of potassium loses its outer electron to convert into a positively charged particle, the potassium ion.

Ions are charged particles into which atoms of elements are converted when they lose or gain electrons.

The charge of an ion is determined by the number of electrons that a given atom gains or loses. The ions can thus be positively or negatively charged and are designated by the signs '+' and '−' respectively:

$$Na^+,\quad Cl^-,\quad Mg^{2+},\quad Al^{3+}$$

Chemical bond that arises between ions is called ionic.

An ionic bond depends on the attraction that arises between oppositely charged ions. Ionic bond is characteristic of chemical compounds that are formed by combination of elements with strongly differing chemical nature, namely typical metals and typical nonmetals.

Substances formed by ions are called ionic compounds.

Metal oxides and compounds of metals with the halogens (metal halides) are examples of ionic compounds. The properties of metals thus depend on the readiness with which they lose their outer electrons and the properties of nonmetals, on the facility with which they gain electrons to complete their outer layers.

?

1. How do (a) chemical inertness of the noble gases, (b) chemical activity of other elements, (c) chemical properties of metals, and (d) chemical properties of nonmetals, depend on the structure of the atom?

△

2. Why do the metallic properties of elements decrease and their nonmetallic characters increase across the periods with their increasing atomic number and do likewise across the main subgroups with decreasing atomic numbers?
3. Unlike metals, crystals of ionic compounds do not conduct electricity. Why?
4. What is an ionic bond?
5. Compare the structure of the Mg^{2+} and F^- ions with the structure of the atom of neon.
6. Suppose we remove one proton from the nucleus of argon atom and leave its electron shell unchanged. What name shall we now give to such a modified argon atom?

8.5 Oxidation Number (State)

If we compare the electron formulas of a polar covalent compound HCl and an ionic compound NaCl (Fig. 8.3) it will be seen that compounds with polar covalent bonds are formed similarly to ionic compounds: in both cases the outer electron layer is completed at the expense of electrons that are gained from the atoms of the other element. But in compounds with polar bonds the electrons are only displaced toward one element while in ionic compounds they are completely captured by this element. The polar bond is thus intermediate between the nonpolar and ionic.

There is no distinct boundary line between polar and ionic bonds. And it is only a convention to say that an atom, from which the electrons are displaced, 'loses' its electrons (although the bond may be polar covalent and not ionic) and that the other atom, which attracts these electrons, 'gains' them. The charge of the ion in an ionic compound and the conventional charge of the atom in a polar covalent compound is called the *oxidation number* (*oxidation state*).

The oxidation number of an element expresses the number of electrons partly or completely displaced from one atom toward the other in a compound. If an atom loses its electrons its oxidation number is positive and if it gains electrons its oxidation number is negative, just like with ions in ionic compounds. Sodium and hydrogen, for example, have positive oxidation states in sodium chloride, hydrogen halides and water, which are 1+, while the halogen (chlorine) and oxygen have negative oxidation numbers of 1− and 2− respectively. The sign "+" or "−" is placed after the figure describing its charge, for example, Al^{3+}, S^{2-}, Cl^-, Na^+.

The oxidation number of atoms in the molecules of simple substances is zero.

When writing formulas of compounds the symbol of the element that gives off its electrons would usually be written first. The naming of binary compounds is simple: first comes the name of the least electronegative element, followed by the stem of the name of the more electronegative element with the appropriate suffix: $Na^{1+}Cl^{1-}$ is called sodium chloride, $Na^{1+}H^{1-}$ is called sodium hydride, etc.

Let us learn how to determine oxidation numbers of elements and to name compounds from their formulas. Take Ag_2S as an example.

1. First decide which of the two elements has gained electrons. In our case this is sulphur because its chemical symbol comes second.

2. Determine the number of electrons gained by the sulphur atom. Sulphur stands in the sixth group and its outer layer is therefore occupied by six electrons. Two electrons are missing to complete the octet. This means that sulphur gains two electrons and its oxidation number is 2−.

3. The same number of electrons was given off by silver. The number of silver atoms in the molecule is two, and this means that each silver atom has lost one electron. The oxidation number of silver in this compound is 1+.

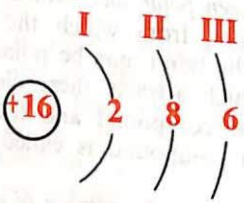
Superscribe the found oxidation numbers above the chemical symbols of the elements: $Ag_2^{1+}S^{2-}$.

4. Now let us give the name to this compound according to the sequence mentioned:

(name of the metal)	(stem of nonmetal)	(suffix)
silver	sulph	-ide

which gives 'silver sulphide'.

Now we can understand why the oxidation number of many elements is variable. Sulphur, for example, has the oxidation number 2 − in its compound with hydrogen H_2S and 6 + in its higher oxide SO_3. The structure of the sulphur atom is



Sulphur stands to the right of hydrogen and to the left of oxygen in the series of electronegativity (see page 70). This means that when sulphur combines with hydrogen the electrons will be drawn off from the hydrogen atom toward the sulphur atom, whereas in the compound of sulphur with oxygen, from the sulphur atom toward the oxygen atoms. In the former case the sulphur atoms gain and in the latter lose electrons.

The sulphur atom needs two electrons to complete its outer layer and it takes them from two hydrogen atoms. The formula of hydrogen sulphide is $H_2^{1+}S^{2-}$ and the oxidation number of sulphur in this compound is 2 −.

When sulphur combines with oxygen, sulphur itself gives off its six outer electrons to the oxygen atoms to complete their outer layers (two electrons to each atom). The formula of the higher sulphur oxide is $S^{6+}O_3^{2-}$ and the oxidation number of sulphur in the oxide is 6 +.

But atoms of many elements can give off only part of their outer electrons and then their oxidation numbers are lower. Sulphur, for example, burns in oxygen or air to give the oxide $S^{4+}O_2^{2-}$ in which its oxidation number is only 4 +, i.e. its atoms give off only four out of the six outer electrons.

Thus one and the same element may exhibit this or that oxidation number depending on whether it gives off or gains electrons. The number of electrons that a given element may gain is equal to the number of electrons that are required to complete the outer layer, but the number of electrons that an atom of an element may lose varies – the outer layer may lose all its electrons or only a part of them. Whether an atom gives off or gains electrons depends on the position of the combining elements in the series of electronegativity: elements which stand to the left will always give off their electrons to the elements that stand to the right of them.

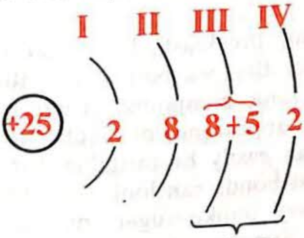
Making use of the electronegativity series and the atomic structure, one can derive formulas of compounds just as we did from the given valencies of elements. The prerequisite condition is that the *donating atom* (the atom which gives off its electrons) loses all its electrons from the outer layer. In other words, it should exhibit its higher valency. Formulas are derived in three steps. Consider an example of the derivation of a formula for a compound of nitrogen with silicon.

1. Write the symbols of the elements in the order in which they stand in the electronegativity series. In our case this order is SiN, i.e. first comes the element giving off its electrons.

2. Once we know the structure of the atoms, we can superscribe the oxidation numbers: $Si^{4+}N^{3-}$ (silicon atoms give off all electrons from their outer layers, and the nitrogen atoms accept that number of electrons which is necessary to complete their outer layers).

3. Subscribe figures indicating the number of atoms of each element in the compount: $Si_3^{4+}N_4^{3-}$. This is the formula of silicon nitride.

The elements standing in the secondary subgroups in which the penultimate layers of their atoms are filled, like the elements of the main subgroups, exhibit their higher oxidation numbers which are equal numerically to the number of the group, though their outer layers contain only two electrons. This is explained by the fact that in addition to the electrons of the outer layer, electrons of the penultimate layer (if their number exceeds eight) may also act as valency electrons. Take manganese, for example (at. No. 25):



?

△

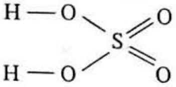
1. What common features can be found in the formation of all types of chemical bonds?
2. What two types of covalent bonding do you know?
3. What do polar covalent and ionic bonds have in common and how do they differ?
4. What compounds are characterized by the presence of only nonpolar covalent bonds and polar covalent bonds?
5*. Look at Fig. 8.4 and draw electron-dot and structural formulas of the molecule of hydrogen peroxide. Calculate the number of electrons that are involved in the formation of bonds between the atoms.
6. Derive formulas for the following compounds: (a) aluminium carbide (compound of aluminium and carbon), (b) carbon nitride (compound of carbon with nitrogen), (c) iodine fluoride, and (d) a

higher oxide of chlorine. The element giving off its electrons in the above compounds exhibits its higher oxidation number.

7*. Derive the formulas of: (a) a nonvolatile compound of calcium with hydrogen (calcium hydride), and (b) the higher oxide of xenon.

8. Consult the electronegativity series (page 70) and derive the formulas of compounds of all elements that stand in the third period with hydrogen.

9. The structural formula of sulphuric acid is



Determine the oxidation number of each element in the acid.

10. Superscribe oxidation numbers in the formulas of the following compounds: (a) ClF_3, (b) SF_6, (c) I_3N, (d) NO_2, (e) SiO_2, (f) XeO_4, and (g) IF_7. Nonpolar bonds are absent in the above compounds. Name the compounds.

8.6 Crystal Lattice

Description of any element normally begins with its physical properties, and on these depends its aggregation state in normal conditions: solid, liquid, or gaseous. A question arises as to what effect the nature of chemical bonds of a substance has on its physical properties. For example, can the character of chemical bonds between particles of a given substance be determined from the appearance of a substance?

Every morning we begin with our breakfast. The sugar that we use to sweeten our tea, and also the water that we boil in a kettle, are covalent compounds, while table salt is an ionic compound. There are no signs by which we could determine from the appearance of a substance whether it is ionic or covalent. Common salt can easily be mistaken for sugar! On the other hand substances with covalent bonds can look very different from one another. For example, water is very unlike sugar; nevertheless, both are compounds with covalent bonds. Simple substances are substances with covalent bonds, but their properties may be very different from one another: diamond (the simple substance of carbon), is the hardest substance known on the earth, and it is very unlike hydrogen which is gas that can only be liquefied and solidified at very low temperatures (when the motion of molecules is practically discontinued).

In order to understand the cause of this variety in the properties of substances it is necessary to get acquainted with the structure of their crystals. Consider the following experiment. Place a handful of peas on a dish with a concave bottom and shake it slightly. The peas will immediately form a pattern shown in Fig. 8.5.

When substances solidify, their component particles will not gather at random but will form a regular pattern which is known as the *crystal lattice* (from the resemblance to the intersections in any lattice). Depending on the nature of the particles that form a crystal lattice, three types are distin-

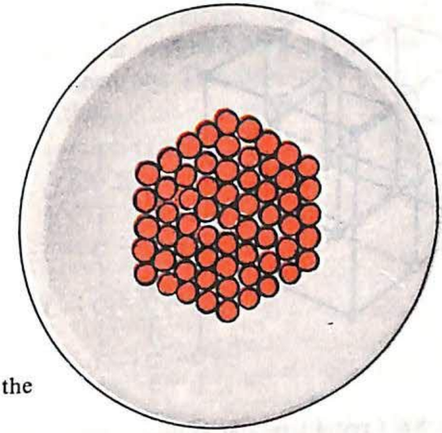


Fig. 8.5 Peas forming a hexagon in the depression of a saucer after shaking

guished: (1) ionic lattices consisting of ions, (2) molecular lattices, consisting of molecules, and (3) atomic lattices consisting of atoms.

Consider the *ionic crystal lattice* in detail, using sodium chloride as an example. Molecules of sodium chloride can only exist at very high temperatures (as vapour of common salt). The white smoke that we observe during combustion of sodium in chlorine is not molecules of sodium chloride but fine crystals of this substance. Crystals of table salt, like those of all other compounds with ionic bonds, are not composed of molecules but of ions that are arranged as shown in Fig. 8.6.

In sodium chloride each negative ion of chlorine (i.e. the chloride ion) is surrounded by the sodium ions and conversely, a positively charged sodium ion is surrounded by the chloride ions, just like the black and white squares of a chessboard. This arrangement is due to the electrostatic forces of attraction and repulsion between oppositely and similarly charged ions.

Oppositely charged ions (Na^+ and Cl^-) are attracted while ions bearing the same charges (Na^+ and Na^+ or Cl^- and Cl^-) are repelled from one another. By the attraction forces the particles tend to approach one another; the repulsion forces separate them as far as possible from each other. These forces thus account for the chessboard arrangement of the ions. Each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions.

The orderly arrangement of ions accounts for the regular shapes of crystals in ionic compounds, while their strength depends on the strength of attraction forces that arise between oppositely charged ions (Fig. 8.7). All ionic compounds are relatively hard, have high melting points and are nonvolatile substances.

Iodine is an example of substances with a *molecular lattice*. We can easily distinguish molecules consisting of pairs of atoms in the crystal lattice of iodine (Fig. 8.8).

An example of a substance with an *atomic crystal lattice* is diamond (Fig. 8.9). As in the crystal lattice of common salt we do not distinguish

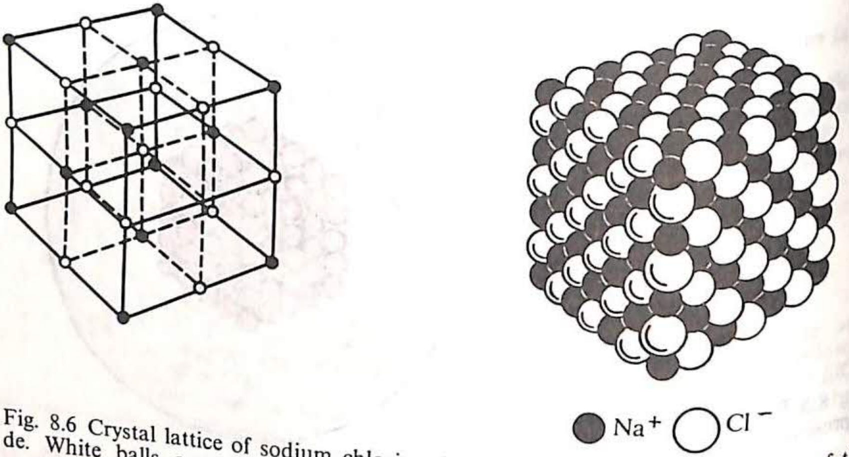


Fig. 8.6 Crystal lattice of sodium chloride. White balls are chloride ions and black, the ions of sodium. Points of the crystal lattice are shown to the left

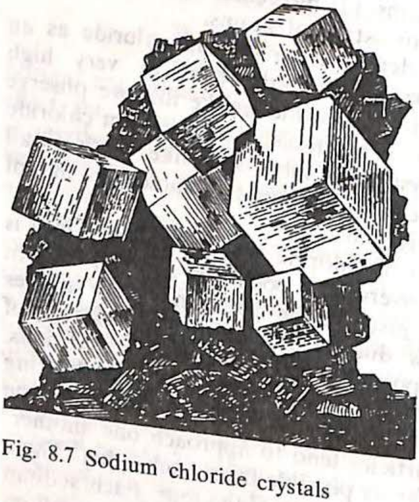


Fig. 8.7 Sodium chloride crystals

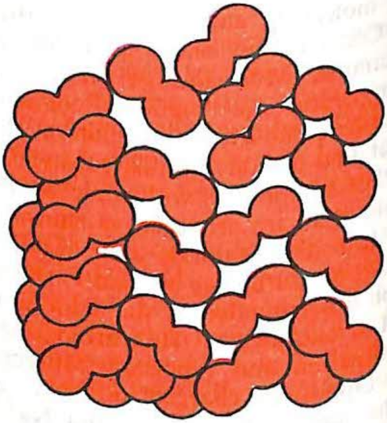


Fig. 8.8 Crystal lattice of iodine

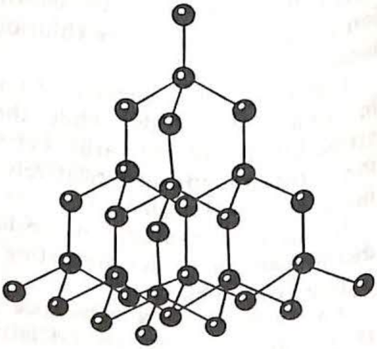
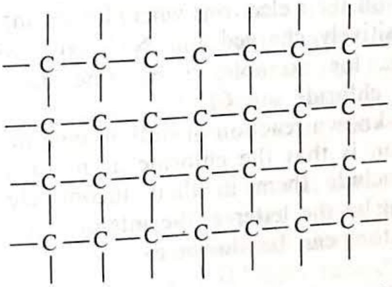


Fig. 8.9 Crystal lattice of diamond. The circles designate the centres of the carbon atoms and lines show covalent bonds

molecules in it: diamond consists of carbon atoms each of which is interconnected by covalent bonds with four neighbouring atoms that are found at the vertices of a regular tetrahedron. The structural formula of diamond can therefore be drawn like this:



It is impossible to break a crystal of diamond without breaking the chemical bonds between its atoms. The crystal is like a gigantic molecule.

Let us again use the example of the peas. The cause of orderly arrangement of the peas on the dish is the force of gravity that makes the peas assume the lowest possible position at the centre of the dish. In the case of the crystal lattice, the role of the gravity force is performed by the force of mutual attraction between ions in ionic, atoms in atomic, and molecules in molecular lattices. The stronger the attraction force, the stronger the crystal lattice, and the more difficult it is to melt the substance or turn it into the gaseous state.

The force of attraction between molecules is much weaker than that between ions or atoms which are joined by covalent bonds. It is easy to guess that substances with molecular lattices will melt and become volatile more easily than substances with ionic or atomic lattices. In fact, all substances that are liquid or gaseous under normal conditions, have molecular lattices in the solid state (for example water in the form of ice, or carbon dioxide in the form of 'dry ice'). There are, however, substances with molecular lattices that are solid under normal conditions, e.g. sugar, iodine, camphor. But they are either low-melting (sugar) or volatile (iodine, camphor). The hardest substances with the highest-melting points that are indispensable in modern technology, can only be found among substances with atomic lattice.

? 1. What are physical properties of substances with (a) molecular, and (b) atomic crystal lattices?

△ 2. By what signs can (a) naphthalene and (b) ice be identified as substances with a molecular crystal lattice?

3. If we mix black and white balls they will assume their position at random: black balls next to white balls, black balls next to black balls, and white balls next to white balls. Why is this random arrangement impossible with ions?

4. The compounds NaCl, AlP and MgS crystallize in lattices with almost the same spacing between positive and negative ions. Which of these compounds is the hardest and melts at the higher temperature? Explain your answer.

8.7 Oxidation-Reduction Reactions

When we studied ionic chemical bonds we stated that metal atoms give off their valency electrons to atoms of nonmetals. Where do atoms give off their electrons when, for example, a sodium atom is converted into a positively charged ion Na^+, and where do atoms take electrons from when, for example, a chlorine atom is converted into a negatively charged chloride ion Cl^-?

Consider again the known reaction of sodium combustion in chlorine. The essence of the reaction is that the chlorine atoms gain the outer electrons from sodium and include them in their incomplete outer layer. If we designate the electron by the letter $\bar{e}$, the interaction of each sodium atom with each chlorine atom can be shown as

$$\overbrace{\mathrm{Na} + \mathrm{Cl}}^{e^-} = \mathrm{Na}^{+1}\,\mathrm{Cl}^{-1}$$

When making out the equation for the reaction, the number of atoms contained in the chlorine molecule should be taken into account. The equation will then be modified as follows:

$$\overbrace{2\,\mathrm{Na} + \mathrm{Cl}_2}^{2e^-} = 2\,\mathrm{Na}^{+1}\,\mathrm{Cl}^{-1}$$

When magnesium burns in oxygen the Mg^{2+} ions and O^{2-} ions are attracted to one another to form magnesium oxide $Mg^{2+}O^{2-}$. The equation of this reaction is:

$$\overbrace{2\,\mathrm{Mg} + \mathrm{O}_2}^{4e^-} = 2\,\mathrm{Mg}^{+2}\mathrm{O}^{-2}$$

Superscribe the oxidation number of each element:

$$2\mathrm{Na}^0 + \mathrm{Cl}_2^0 = 2\mathrm{Na}^{1+}\mathrm{Cl}^{1-}$$

$$2\mathrm{Mn}^0 + \mathrm{O}_2 = 2\mathrm{Mg}^{2+}\mathrm{O}^{2-}$$

At the beginning of this course in chemistry, when we studied reactions of elements with oxygen, we learnt that elements are oxidized by oxygen. But when metals react with chlorine or other nonmetals the same reaction occurs: electrons are attracted by the atoms of nonmetals from the atoms of metals. Therefore it was assumed that (1) all reactions in which electrons pass from one element to another be called *oxidation-reduction reactions*; (2) the element giving off (donating) electrons be referred to as a *reductant* since it is oxidized and the element gaining (accepting) the electrons be called the *oxidant* since it is reduced. Metals give off their electrons and are thus oxidized: they therefore act as reductants. In reactions between metals and oxygen the latter acts as an oxidant, and in reactions of metals with the halogens, the halogens are oxidants.

Consider now the known reaction of copper oxide reduction with hydrogen

$$\overset{\xleftarrow{\quad 2\bar{e}\quad}}{\mathrm{Cu}^{2+}\mathrm{O}^{2-} + \mathrm{H}_2^0} = \mathrm{Cu}^0 + \mathrm{H}_2^{1+}\mathrm{O}^{2-}$$

Superscribe the oxidation number for each element and underline the symbols of those elements in which the oxidation number has changed during the reaction. In our case these are copper and hydrogen. The reaction can therefore be called an oxidation-reduction reaction. The direction of the electron transfer is indicated by the arrow: they move from the hydrogen atoms to the copper ions.

The copper ions Cu^{2+} have turned into neutral atoms. Two electrons were needed in the copper ion in order to convert it into the atom. The copper ions have accepted these two electrons and turned into copper atoms. Electrically neutral atoms of hydrogen H^0 have turned into H^+ ions, since they lost one electron each. The electrons have moved from the hydrogen atoms toward the ions of copper. The element copper is reduced in this reaction while the element hydrogen is oxidized.

These are the main and essential characteristics of the reaction in question. Having lost their charges, the copper atoms stopped attracting the oxygen ions and copper was liberated in the free state. Once the hydrogen has acquired a positive charge it attracts the negatively charged oxygen ion to form a water molecule. The ionic bond has converted into the polar covalent bond.

The oxidant accepts electrons in order to reduce itself while the reductant gives off its electrons to be oxidized.

Metals in the free state always act as reductants while nonmetals (except fluorine which is always an oxidant) can act as both oxidant or reductant; for example in the reaction $\mathrm{S}^0 + \mathrm{H}_2^0 = \mathrm{H}_2^{1+}\mathrm{S}^{2-}$ sulphur is the oxidant and in the reaction $\mathrm{S}^0 + \mathrm{O}_2^0 = \mathrm{S}^{4+}\mathrm{O}_2^{2-}$ sulphur acts as a reductant.

When making out equations of oxidation-reduction reactions the coefficients are selected with the following consideration in view: the number of electrons accepted by the atoms (ions) of the oxidizing element is equal to the number of electrons given off by the atoms (ions) of the reducing element. We are given, for example, the following:

$$\mathrm{SO}_2 + \mathrm{H}_2\mathrm{S} \rightarrow \mathrm{S} + \mathrm{H}_2\mathrm{O}$$

Find their oxidation numbers from the formula, and superscribe them above the chemical symbols of elements

$$\mathrm{S}^{4+}\mathrm{O}_2^{2-} + \mathrm{H}_2^{1+}\mathrm{S}^{2-} \rightarrow \mathrm{S}^0 + \mathrm{H}_2^{1+}\mathrm{O}^{2-}$$

The oxidation number has only changed in the sulphur atoms: in sulphur(IV) oxide it has changed from 4+ to 0 and in hydrogen sulphide from 2− to 0. Let us describe the transition of electrons in this reaction as follows:

$$\begin{array}{l|l} \mathrm{S}^{4+} + 4\bar{e} = \mathrm{S}^0 & 1 \\ \mathrm{S}^{2-} - 2\bar{e} = \mathrm{S}^0 & 2 \end{array}$$

The number of electrons given off by the S^{2-} ions should be equal to the number of electrons accepted by the S^{4+} ions. It means that each S^{4+} ion (i.e. each molecule of sulphur(IV) oxide) will interact with two S^{2-} ions (two molecules of hydrogen sulphide). Put figures 1 and 2 to the right of the vertical line. These are the coefficients for the formulas of the substances involved. Put them in the equation to obtain the following:

$$S^{4+}O_2^{2-} + 2H_2^{1+}S^{2-} = 3S^0 + 2H_2^{1+}O^{2-}$$

Oxidation numbers of elements with variable valencies can be similarly found if oxidation numbers of the other elements involved are known. For example, in the salt $Na_2^{1+}SO_3^{2-}$ the oxidation numbers of oxygen (2 –) and sodium (1 +) are given. Three oxygen atoms have received $2 \times 3 = 6$ electrons; of this number 2 electrons were gained from the sodium atoms (one electron from each sodium atom) and the other four from the sulphur atom. The oxidation number of sulphur can thus be found. It is 4+ ($Na_2^{1+}S^{4+}O_3^{2-}$).

? △

1. Using the electron theory of chemical reactions consider the following reactions: (1) thermal decomposition of mercury oxide; (2) preparation of hydrogen by acting with hydrochloric acid on zinc. Which element is (a) oxidized, (b) reduced; and which element is (c) an oxidant and (d) a reductant?

2. Using the rule given in the text, write equations for the following reactions:

(a) $S + H_2SO_4 \rightarrow SO_2 + H_2O$

(b) $Cl_2 + KI \rightarrow I_2 + KCl$

(c) $Al + Br_2 \rightarrow AlBr_3$

(d) $Cl_2 + H_2O \rightarrow HCl + HClO$

(e) $KClO_3 \rightarrow KCl + O_2$

(f) $CuCl_2 + Fe \rightarrow FeCl_2 + Cu$

9 The Halogens

9.1 General Characteristics of the Halogens

Let us remember what are the characteristic features of nonmetals: they stand at the end of the periods in the periodic table (see colour plate III). Except in the inert gases, the outer electron layer of their atoms is incomplete but is nearing completion. The atoms of nonmetals should therefore accept electrons when they combine with elements whose atoms readily give off their electrons. These other elements are metals and hydrogen. Reactions with metals and hydrogen are therefore more characteristic of nonmetals.

Nonmetals exist in the form of negatively charged ions in compounds with typical metals. These compounds have the ionic crystal lattice and are therefore hard substances with high melting points.

In compounds with hydrogen, nonmetals are connected with hydrogen by a polar covalent bond, and the crystal lattice of these compounds is molecular. In normal conditions these compounds are either gases (like hydrogen halides) or volatile liquids (like water).

The nonmetal character is most pronounced in the halogens. They make up the main subgroup of group VII in the periodic system of chemical elements. Their outer layers contain 7 electrons. One *p* electron is unpaired and only one more electron is required to complete the outer layer. In compounds with hydrogen and metals the halogens therefore always exhibit the oxidation number of 1−. Being the most electronegative chemical element fluorine has an oxidation number of 1− in all its compounds (not only in compounds with hydrogen and metals). The other halogens may, however, exhibit positive oxidation numbers up to 7+, for example, in their compounds with oxygen.

?

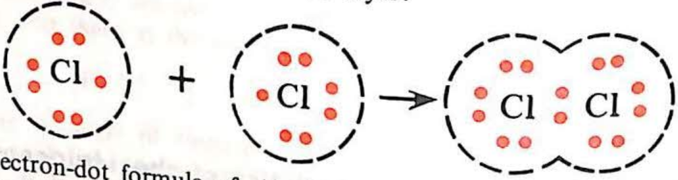
1. What is the difference between the halogen compounds with hydrogen and their compounds with typical metals? Consider (a) their chemical bonds, (b) the structure of their crystal lattice, (c) their physical properties.

9.2 Chlorine

The chemical symbol of chlorine is Cl. Its atomic weight is 35.5, the charge of the nucleus, +17.

The chemical formula of chlorine is Cl_2.

The outer layer of the chlorine atom (like that of the other halogens) contains 7 electrons. The chlorine atom can accept the missing electron by sharing an electron pair with the other chlorine atom; then each of the two atoms has eight electrons in its outer layer:



The electron-dot formula of chlorine molecule is $:\underset{..}{\ddot{\text{Cl}}}:\underset{..}{\ddot{\text{Cl}}}:$ while its structural formula is Cl—Cl. Crystals of solid chlorine are composed of diatomic molecules that are held together by intermolecular attraction whose force is so weak that they can only exist at low temperatures. Under normal conditions chlorine is a gaseous substance. It is a yellow-green gas with a pungent odour. Its molecular weight is $35.5 \times 2 = 71$, and its density relative to air is $71 : 29 = 2.45$. Chlorine is almost twice heavier than air. It is readily soluble in water. An aqueous solution of chlorine is called chlorine water. It preserves the colour and odour of chlorine.

Inhalation of chlorine causes suffocation and may even cause death. It should therefore be smelt only after taking all precautions.

The addition reactions with hydrogen and metals are characteristic of chlorine (as of the halogen). It acts as an oxidant in these reactions, as in the known reaction of sodium combustion in chlorine

$$\overset{2e^-}{\overrightarrow{2\text{Na} + \text{Cl}_2}} = 2\text{Na}^{+1}\text{Cl}^{-1}$$

Other metals react with chlorine in the same way. When iron powder is heated in a spoon and discharged into a flask containing chlorine, the metal particles become white-hot before they reach the bottom of the flask because of their reaction with chlorine. The flask becomes filled with a brown smoke which consists of minutest particles of the reaction product, ferric chloride FeCl_3

$$\overset{6e^-}{\overrightarrow{2\text{Fe} + 3\text{Cl}_2}} = 2\text{Fe}^{+3}\text{Cl}_3^{-1}$$

If powdered antimony is discharged into the chlorine atmosphere without preliminary heating, the same sparkling shower will be observed (Fig. 9.1) and the bottle will be filled with a white smoke of antimony(III) chloride SbCl_3

$$\overset{6e^-}{\overrightarrow{2\text{Sb} + 3\text{Cl}_2}} = 2\text{Sb}^{+3}\text{Cl}_3^{-1}$$

If we heat a coil of fine copper wire and immerse it in the atmosphere of chlorine gas, copper will become white-hot and burn (Fig. 9.2) to fill the bottle with a brown smoke consisting of copper(II) chloride CuCl_2 particles

$$\overset{2e^-}{\overrightarrow{\text{Cu} + \text{Cl}_2}} = \text{Cu}^{+2}\text{Cl}_2^{-1}$$

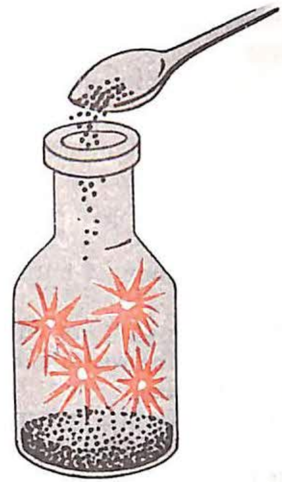


Fig. 9.1 Burning antimony in chlorine

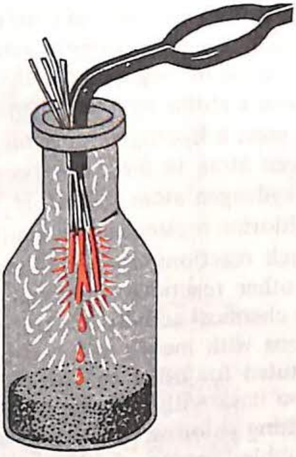


Fig. 9.2 Burning copper in chlorine

Chlorine acts as an oxidant in the known reaction with hydrogen. Hydrogen combustion in chlorine is shown in Fig. 9.3

$$\overbrace{\mathrm{H_2} + \mathrm{Cl_2}}^{2e^-} = 2\mathrm{H}^{+1}\mathrm{Cl}^{-1}$$

This reaction can occur in a different way. If chlorine is mixed with hydrogen in a thick-walled cylinder (covered with a piece of cardboard) and a ribbon of magnesium is lighted near the cylinder, the gaseous mixture will

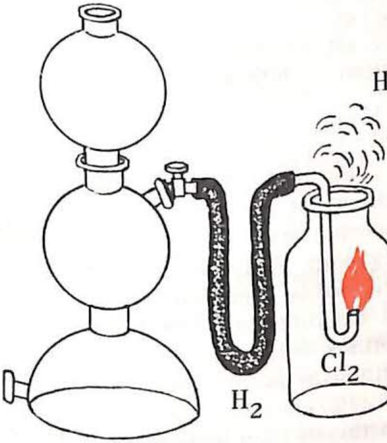


Fig. 9.3 Burning hydrogen in chlorine

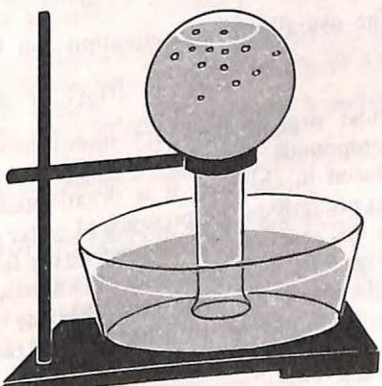


Fig. 9.4 Displacement of oxygen from water by chlorine

explode loudly. Bright light induces the explosion, just as an electric spark explodes a mixture of hydrogen and oxygen.

The reaction begins with the splitting of chlorine molecules into their component atoms by the energy of light or by heat ($Cl_2 = 2Cl$); the chlorine atoms meet a hydrogen molecule and each chlorine atom combines with one hydrogen atom to form a molecule of hydrogen chloride and to release the other hydrogen atom ($Cl + H_2 = HCl + H$); the hydrogen atoms react with chlorine molecules in a similar way ($H + Cl_2 = HCl + Cl$), and so on. Such reactions are called *chain reactions*. The reaction of burning and some other reactions are chain reactions.

The chemical activity of chlorine as an oxidant shows itself not only in its reactions with metals and hydrogen but also in reactions where chlorine is substituted for other nonmetals, e. g. for oxygen in water.

Fill a flask with chlorine water to its full capacity, overturn it into a dish containing chlorine water (Fig. 9.4) and keep it in this position for a while: gas bubbles appear on the flask walls. This gas is oxygen. It accumulates in the upper portion of the flask; the solution gradually loses its colour and the odour of chlorine is no longer smelt. Blue litmus turns red in the solution

$$Cl_2^0 + H_2O = HCl^{1-} + HCl^{1+}O$$

$$Cl^0 + 1\bar{e} = Cl^{1-}$$

$$Cl^0 - 1\bar{e} = Cl^{1+}$$

It will be seen from the electron equations that some chlorine atoms oxidize other chlorine atoms. The products of such oxidation are acids in which chlorine may have the negative oxidation number (HCl) and positive oxidation number (HClO). The latter acid is called hypochlorous. It is very unstable. On decomposing it liberates oxygen

$$2HClO = 2HCl + O_2 \uparrow$$

The overall reaction equation can be written as follows:

$$2Cl_2 + 2H_2O = 4HCl + O_2$$

Most organic dyes are discoloured by chlorine to turn into colourless compounds. If a piece of paper stained with violet ink or litmus solution is placed in chlorine, it is discoloured (bleached) very rapidly. But bleaching occurs only in the presence of water or its vapour. Water serves as a catalyst in this reaction. A coloured textile fabric will not be bleached in dry chlorine (Fig. 9.5). The presence of water vapour activates chlorine toward other substances as well. Dry chlorine at normal temperature does not act, for example, on iron but it will react with iron in the presence of water vapour.

We know now that chlorine is an extremely active nonmetal. It can displace oxygen from such stable compounds as water in the presence of light, and it is especially active in reactions with metals and hydrogen. In its

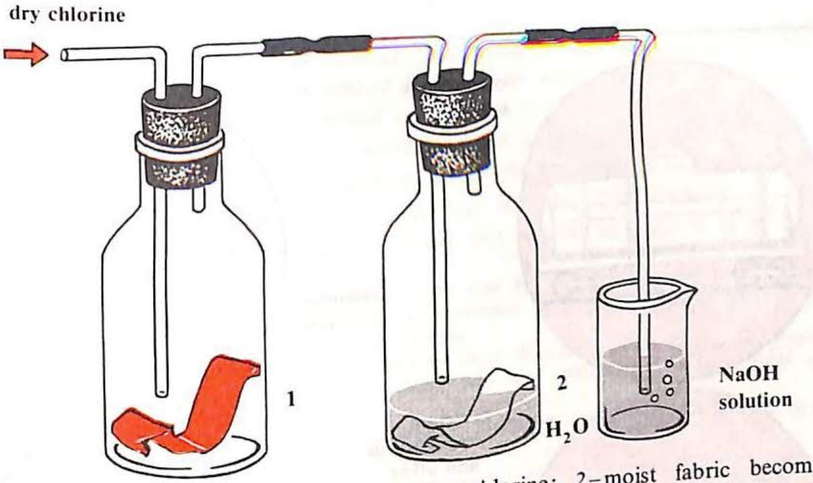


Fig. 9.5 Discolouration of dyes: *1*–dry coloured textile fabric is not discoloured by chlorine; *2*–moist fabric becomes colourless

compounds with metals and hydrogen, chlorine exhibits the oxidation number of 1 – .

?
△

1. Describe the physical properties of chlorine. How does chlorine differ in its appearance from all other gases which are known to you?
2. What are the densities of chlorine and carbon dioxide relative to air?
3. A standard cylinder contains 30 kg of liquid chlorine. What volume will 30 kg of chlorine occupy under normal conditions?
4. Describe the chemical properties of chlorine. Write reaction equations.
5. If litmus solution is poured into a freshly prepared chlorine water its colour vanishes but if chlorine water stands in the light for a long time, the litmus turns red. Explain.
6. Why should chlorine be dried thoroughly before it is packed in steel cylinders?

9.3

Occurrence of Chlorine in Nature and Its Uses

Chlorine is used for disinfection of potable water. Before water is delivered to its consumers through the water-supply system it is chlorinated by dissolving a small amount of chlorine in it: this kills almost all bacteria contained in the water.

Chlorine is used for bleaching textile fabrics and paper, and for industrial manufacture of bleaching powders. Before chlorine was discovered, the sun's rays and air were used for bleaching purposes. Bleaching continued for

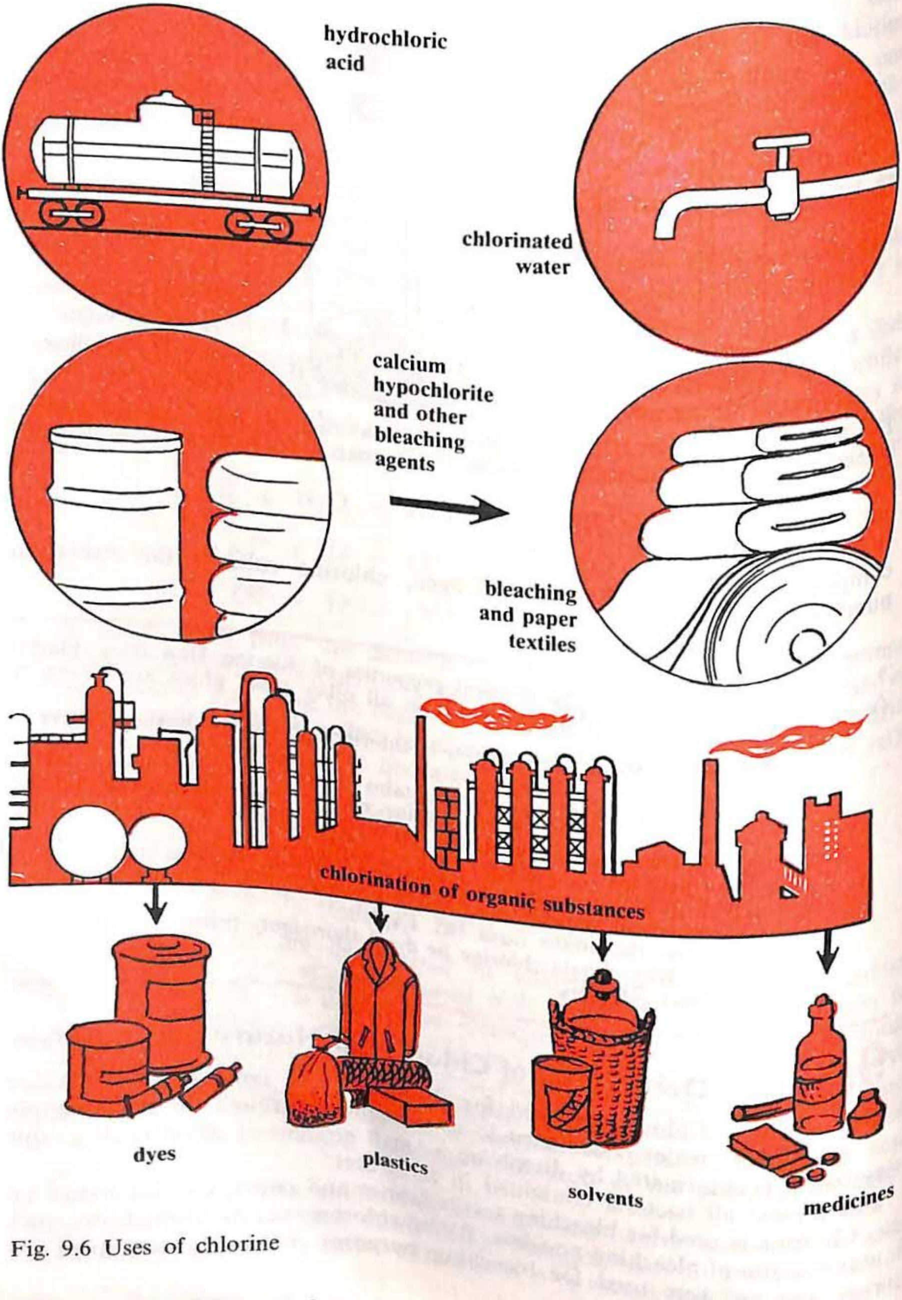

hydrochloric acid
chlorinated water
calcium hypochlorite and other bleaching agents
bleaching and paper textiles
chlorination of organic substances
dyes
plastics
solvents
medicines

Fig. 9.6 Uses of chlorine

months and large areas were required to unroll linen or other fabrics in the open air. Now bleaching in solutions takes only a few hours.

Chlorine does not occur in nature in the free state because of its high activity. The most abundant chlorine compound is sodium chloride which is contained in sea water, and it is recovered on a commercial scale from salt lakes and deposits that were formed in times immemorial (dried salt lakes).

Sodium chloride is the starting material for the manufacture of free chlorine, and of its compounds that do not occur in nature (Fig. 9.6).

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△

1. What uses of free chlorine and its compounds do you know? Describe the properties of chlorine and of its compounds that account for their practical uses.
2. Imagine that free chlorine was liberated into the atmosphere. By what chemical reactions will the atmosphere clear itself of chlorine?
3. What is the most abundant chlorine compound in nature that can be found in any home?

9.4

Hydrogen Chloride

Hydrogen chloride is one of the most important compounds of chlorine that are produced artificially. Hydrogen chloride HCl is a suffocating gas, its density relative to air is slightly above 1.

Fill a cylinder with hydrogen chloride, cover it with a glass plate and put it upside down into a dish filled with water (Fig. 9.7). Remove the glass plate: water quickly rises in the cylinder because the hydrogen chloride dissolves and water is forced into the rarefied space by atmospheric pressure. The cylinder now contains hydrochloric acid. Test it with litmus.

Hydrogen chloride is one of the most readily soluble gases: one litre of water can dissolve up to 500 litres of hydrogen chloride (at room temperature).

Hydrogen chloride can be prepared in a chemical laboratory by heating sodium chloride with concentrated sulphuric acid (Fig. 9.8):

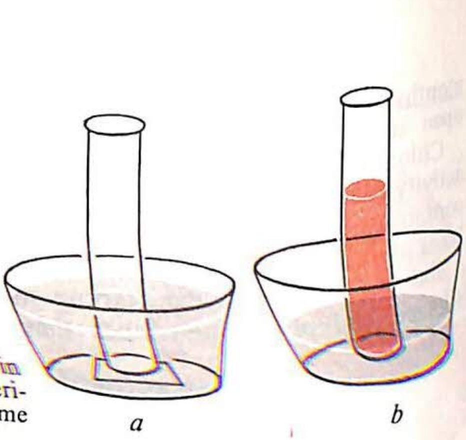
$$2NaCl + \underset{\text{(conc.)}}{H_2SO_4} = Na_2SO_4 + 2HCl\uparrow$$

Hydrogen chloride is heavier than air and it can therefore be collected in a dry flask by displacing the air from it.

When the flask is completely filled with hydrogen chloride, fume appears above the flask's mouth. This fume consists of the minutest drops of hydrochloric acid which has formed by combination of the hydrogen chloride with droplets of water contained in the air.

In industry hydrogen chloride is obtained by *synthesis*, i.e. direct combination of chlorine with hydrogen.

Fig. 9.7 Dissolving hydrogen chloride in water: *a*–at the beginning of the experiment, *b*–in a certain period of time



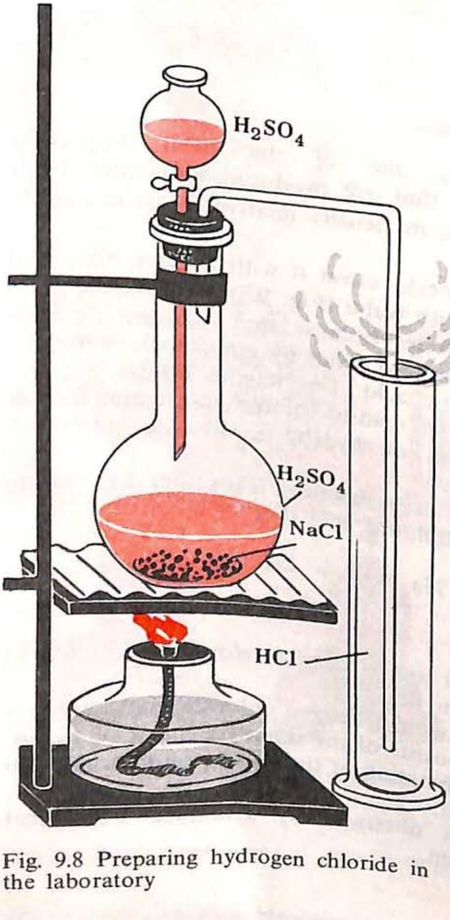


Fig. 9.8 Preparing hydrogen chloride in the laboratory

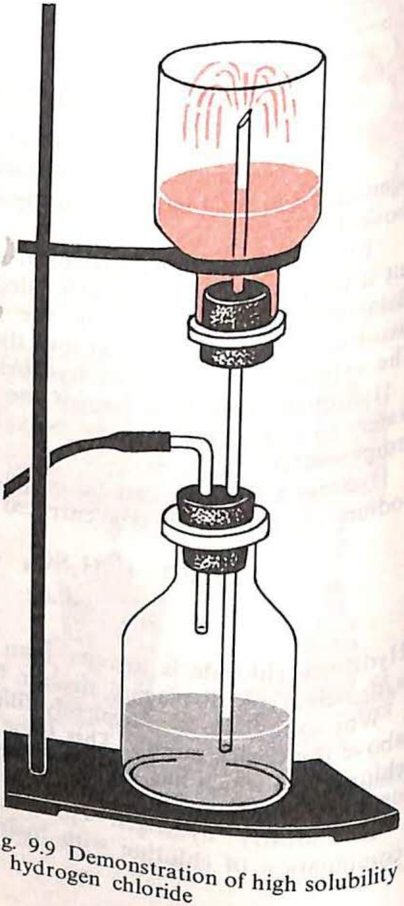


Fig. 9.9 Demonstration of high solubility of hydrogen chloride

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1. Describe the physical properties of hydrogen chloride.
2. How can hydrogen chloride be prepared in a laboratory? Draw the sketch of the apparatus and write the reaction equation.
3. Fill a bottle with hydrogen chloride and close it with a stopper through which passes a glass tube. Overturn the bottle and immerse the tube in another bottle containing a violet litmus solution (Fig. 9.9). Add a few drops of water to the bottle through the tube. Describe your observations.
4*. What is the concentration (g/litre) of 1 litre of hydrochloric acid prepared in the previous experiment? The experiment was carried out under normal conditions.

9.5

Hydrochloric Acid

An aqueous solution of hydrogen chloride is called hydrochloric acid. By saturating water with hydrogen chloride one can prepare a 40 per cent solution of hydrochloric acid (weight fraction of HCl, 40 per cent). Concentrated hydrochloric acid has a pungent odour and 'fumes' in the air.

All metals that come before hydrogen in the electrochemical series, and all basic oxides and hydroxides react with hydrochloric acid to form chlorides, i.e. salts of hydrochloric acid. For example:

$$Zn + 2HCl = ZnCl_2 + H_2\uparrow$$

$$ZnO + 2HCl = ZnCl_2 + H_2O$$

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

Almost all chlorides are soluble in water. Among a few practically insoluble chlorides is silver chloride. It precipitates as white curdy flakes (like coagulated milk) when silver nitrate solution is added to hydrochloric acid or to a solution of any of its salts:

$$HCl + AgNO_3 = AgCl\downarrow + HNO_3$$

$$NaCl + AgNO_3 = AgCl\downarrow + NaNO_3$$

When nitric acid is added, the precipitate does not dissolve because unlike other silver salts, that look similar, silver chloride is insoluble in acids either. Therefore, if silver nitrate precipitates a white substance from an unknown solution and the precipitate is not dissolved by nitric acid, one may be sure that the unknown solution contains hydrochloric acid or its salts.

When exposed to light, silver chloride blackens since it decomposes into chlorine and metallic silver which is liberated as a fine black powder.

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1. Describe the properties of hydrochloric acid.
2. Why does concentrated hydrochloric acid 'fume' in the air?
3. By what experiments can it be proved that hydrochloric acid

contains hydrogen and chlorine? Write equations for the corresponding reactions.

4. Potassium chloride, chlorine, and silver nitrate solutions are placed in three separate test tubes. How can they be identified?

5*. What salt smells of chlorine, changes its colour when kept in the light, and turns white again when chlorine water is added? Write equations for the corresponding reactions. Consider them from the standpoint of the electron theory.

9.6 Uses of Hydrochloric Acid

Hydrochloric acid is widely used in the economy. We shall deal with it very often as well.

Large quantities of hydrochloric acid are used in industry to pickle steel. Articles plated with nickel, tin, and chromium are widely used in everyday life. In order to apply a coat of the protective metal to either steel or iron, their surfaces should be cleaned of iron oxides, otherwise the plating metal will not adhere to them. The oxide films are removed chemically by pickling in hydrochloric or sulphuric acid. The disadvantage of this method is that acid reacts not only with the oxide but with pure metal as well. In order to avoid this, a small portion of an inhibitor is added to the acid. *Inhibitors are substances that retard undesirable reactions.* The acid containing the inhibitor can be kept in steel containers or handled in tank cars.

Hydrochloric acid is available at pharmacy shops. Its dilute solution is prescribed to patients with decreased acidity of their gastric juices (subacidity).

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1. What uses of hydrochloric acid do you know?
2. Ferric chloride $FeCl_3$ is prepared by reacting iron with chlorine, or iron oxide with hydrochloric acid. Write the corresponding reaction equations.
3. What two reactions occur during pickling of iron in hydrochloric acid? Write reaction equations.

9.7 Fluorine, Bromine, and Iodine

In addition to chlorine, the halogen subgroup also contains fluorine, bromine and iodine (Table 7.3, p. 131). Their molecules are also diatomic and their crystal lattice is molecular. The intermolecular forces that hold the molecules within the confinements of the lattice increase with the increasing atomic number of the halogens, and their volatility therefore decreases: in ordinary conditions fluorine, like chlorine, is a gas, bromine is a dark red volatile liquid, and iodine is a grey solid. When heated slightly, iodine converts into a violet vapour without melting. The name iodine is derived from the Greek *iodes*, violet-like. The vapour precipitates on the cold walls of the test tube, in which it is being heated, in the form of crystals. The transition from the solid state into vapour, omitting the melting stage, is called *sublimation*.

Bromine and iodine are sparingly soluble in water but readily soluble in organic solvents. The iodine tincture used at home to treat minor injuries is actually a solution of free iodine in alcohol. Aqueous solutions of bromine (bromine water) and of iodine (iodine water) are both brown. But iodine molecules can be easily identified by using starch with which they combine to form a dark blue product. Of all the substances we know free iodine gives a blue colour only to starch and the latter is therefore used as a reagent for free iodine, i.e. iodine molecules. Iodine in turn is a *reagent* for starch.

Fluorine is the most active nonmetal. It reacts with almost all simple substances and compounds, the inert gases krypton and xenon included. Even water burns in fluorine with a hot flame. The latter reaction consists in substitution of fluorine for oxygen

$$2H_2^{1+}O^{2-} + 2F_2^0 = 4H^{1+}F^{1-} + O_2^0$$

This indicates that fluorine is more active than oxygen. According to their increasing atomic numbers, the halogens form the following series: fluorine (at. No. 9), chlorine (at. No. 17), bromine (at. No. 35) and iodine (at. No. 53). High chemical activity is characteristic of all the halogens. But of any pair of halogens one should be more, and the other less, active. The different activity is most vividly illustrated by substitution of one halogen for another.

Place a solution of sodium bromide in a test tube and add chlorine water. The solution immediately turns a reddish-brown colour, which is characteristic of bromine molecules. Bromine has been substituted by chlorine which is thus separated in the free state:

$$2NaBr + Cl_2 = 2NaCl + Br_2$$

Add chlorine water to potassium iodide solution. The solution also turns reddish-brown. It is easy to prove that this colour is due to molecules of iodine by adding starch solution: the brown solution turns dark blue. Iodine has been substituted by chlorine in potassium iodide and iodine is liberated in the free state:

$$2KI + Cl_2 = 2KCl + I_2$$

Add bromine water to a solution of potassium iodide: the solution turns brown. But this colour may be due either to bromine or iodine. Add starch solution: the brown colour changes to a dark blue which means that free molecules of iodine are present in the solution because neither potassium iodide nor bromine give a colour reaction with starch. Iodine has been substituted by bromine in potassium iodide and iodine is liberated in the free state:

$$2KI + Br_2 = 2KBr + I_2$$

The above experiments show that:

fluorine (at. No. 9) displaces the other halogens from their compounds with hydrogen and metals;

chlorine (at. No. 17) displaces only bromine and iodine;

bromine (at. No. 35) displaces only iodine;
iodine (at. No. 53) does not displace any other halogens.

Compare the order in which the halogens substitute for one another with their position in the periodic system of chemical elements. The halogens with lower atomic numbers will displace any halogen with a higher atomic number, but never reverse.

Consider one of the above reactions of substitution, e.g. chlorine for iodine in potassium iodide, from the standpoint of the electron theory. Iodine is contained in the initial substances in the form of negatively charged ions (in potassium iodide), while chlorine is contained in the form of electrically neutral atoms (in chlorine molecules); the reaction products, on the contrary, contain chlorine as the negatively charged chloride ion, and iodine in the form of atoms:

$$\overbrace{2K^{+}I^{-} + \ Cl_2^{0}}^{2\bar{e}} = 2K^{1+}Cl^{1-} + I_2^{0}$$

The reaction consists of a transition of electrons from the iodine ions to the chlorine atoms. The iodide ions lose electrons, i.e. are oxidized into electrically neutral atoms that join in pairs to form molecules of free iodine. The chlorine atoms accept electrons, i.e. are reduced into negatively charged chloride ions.

While free fluorine is very active chemically, its compounds, on the contrary, are characterized by chemical inertness. A plastic material made of fluorine and carbon (fluoroplastic) is the most stable material with respect to acids, alkalis, oxidants and other chemical reagents. Bromine is indispensable in the manufacture of photographic materials. The photographic process is based on the decomposition of silver bromide on exposure to light. The black image on a developed film is formed by minute particles of free metallic silver. Bromine preparations are used in medicine as sedatives.

Fluorine and iodine are contained in our bodies: fluorine in our teeth and iodine in the form of organic compounds of the thyroid gland. These two halogens are supplied to our bodies with food and water (as salts). The amounts of the halides in food and drinking water are very small but the body's need for these elements is also very low. Fluorine is almost absent from the water of some areas and this causes diseases of the teeth. These diseases are treated with compounds containing fluorine. But excessive quantities of fluorine in drinking water are harmful too. Excess fluorine causes diseases of the teeth as well. Some water lacks iodine compounds and this is harmful for the thyroid gland of man (causing goiter). To prevent this serious disease, the table salt that is delivered to these areas, undergoes special treatment with iodine compounds.

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1. How does the activity of the halogens change with their increasing atomic numbers? How are these changes manifested?
2. Which of the halogens react with (a) potassium chloride, (b) calcium bromide, (c) sodium iodide? Write the reaction equations. What substances are oxidized and what are reduced?

3. By what reactions can the following solutions be identified: (a) sodium chloride, (b) sodium bromide, (c) potassium iodide?

■

1. Place a few drops of iodine tincture in a test tube and heat slightly. Using water colour paint, try to find the hue that matches the colour of the vapour evolved from the iodine tincture. Observe sublimation of iodine crystals.
2. Add a small quantity of water to a few drops of iodine tincture and using the obtained solution detect the presence of starch in various foods. To do this, place a drop of the solution on the cut surfaces of a potato, and a carrot, on flour, a slice of bread, a shelled pea, and a green leaf that was picked in the daytime, etc. Record the results of your observations.

10 Oxygen Subgroup

The halogens form the main subgroup of group VII. One can justly expect that nonmetals belonging to the main subgroup of group VI may have chemical properties similar to those of the halogens. This subgroup is made up of nonmetals with the oxygen in the first box.

Atoms of the elements standing in the oxygen subgroup have 6 electrons in their outer layers: 2 paired *s* electrons, and 4 *p* electrons of which 2 are paired and 2 unpaired. The axes of *p* electron clouds are mutually perpendicular and the covalent bonds formed by them are arranged at an angle of about 100° (Fig. 10.2 *b*). Two electrons are needed to complete the outer layer. The atoms of these elements should react with metals and hydrogen to show a negative oxidation number. Their compounds with typical metals should have the ionic crystal lattice. They must have a high melting point. Their compounds with hydrogen (of the H_2E type), like hydrogen halides, should have molecular crystal lattices and be volatile.

Placed at the beginning of the subgroup, oxygen is the most electronegative nonmetal. All other nonmetals of this subgroup should exhibit a positive oxidation number (up to $6+$) in compounds with oxygen, with which they form oxides of the EO_3 type.

10.1

Oxygen and Ozone. Allotropy

We have already studied the physical and chemical properties of oxygen. The molecules of oxygen are composed of two atoms interconnected by the covalent nonpolar bond, which is formed by two electron pairs.

The atoms of oxygen may form two simple substances: oxygen, which we already know, and ozone, which is new to us.

When an electric discharge is passed through oxygen a specific odour can be smelt. We notice this odour during thunderstorms. This is the odour of ozone (in Greek *ozein* is to smell).

The apparatus for preparing ozone is called an ozonizer (Fig. 10.1). It consists of a glass vessel, round which a metal wire is wound. Inside the vessel there is another metal wire. As oxygen is passed through the vessel; voltage is applied across the wires and oxygen thus moves through an electrical discharge.

The reaction of the formation of ozone can be shown as:

$$3O_2 = 2O_3 - Q$$

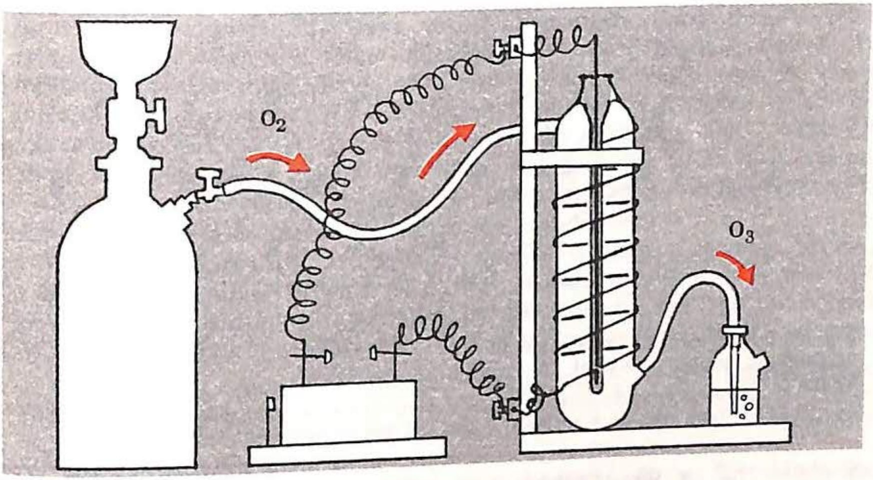

Fig. 10.1 Ozonizer

In ordinary conditions ozone is gas. It is a rather unstable substance and rapidly decomposes into oxygen:

$$2O_3 = 3O_2 + Q$$

For this reason ozone is not accumulated in the atmosphere. The properties of ozone differ from those of oxygen. It is 1.5 times heavier than oxygen and dissolves more readily in water. The chemical activity of ozone is much higher than of oxygen. Oxygen, for example, fails to oxidize silver even at high temperature while ozone oxidizes silver at room temperature to form silver oxide.

When ozone is converted into oxygen, one atom of oxygen is first split off from the ozone molecule:

$$O_3 = O_2 + O$$

The oxygen atoms so formed join in molecules

$$2O = O_2$$

The chemical activity of the split off oxygen atoms is much higher than that of oxygen molecules. Ozone therefore has higher chemical activity than oxygen.

So one element can have more than one simple substance in the free state. This phenomenon is known as *allotropy.*

Allotropy is the ability of atoms of elements to form two and more simple substances (allotropes).

These may differ in the composition of their molecules, in the form of their crystal lattices and, hence, in their properties.

Oxygen and ozone are allotropic modifications of oxygen that differ in the composition of their molecules, and in their physical and chemical properties.

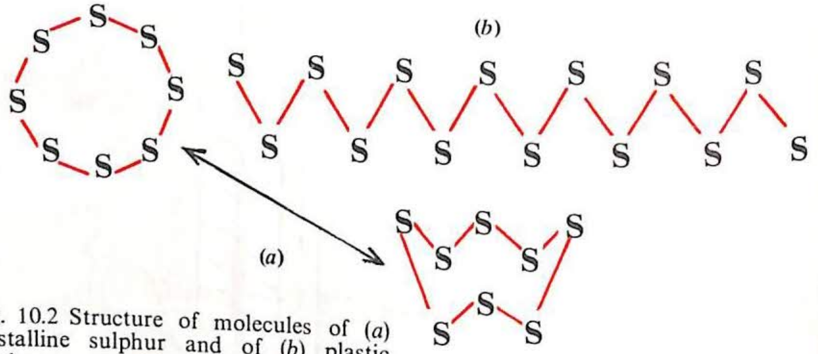

Fig. 10.2 Structure of molecules of (*a*) crystalline sulphur and of (*b*) plastic sulphur

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1. Which number is greater – that of chemical elements or of simple substances?
2. What differences in the properties of oxygen and ozone do you know? Why do their properties differ? Why does ozone discolour some dyes (fuchsine, for example) while oxygen does not?
3. Do you know reactions by which one chemical element may be converted into another, or one simple substance into another?

10.2 Sulphur

The chemical symbol of sulphur is S. Atomic weight of sulphur is 32; the charge of the nucleus, +16.

Among the nonmetals of the main subgroup of group VI of the periodic system, sulphur stands only second to oxygen with respect to its abundance and importance.

The atoms of the halogens can complete their outer electron layers only by combining in pairs. There are no allotropes among them. Sulphur also can form diatomic molecules S=S by bonding the atoms by two electron pairs. But one sulphur atom can spend two valency units to attach two other sulphur atoms to form —S—S—S—S—S—S—S—S— chains that may close in rings (Fig. 10.2 *a*). Like oxygen, sulphur can form allotropes.

Free sulphur occurs in nature as golden-yellow transparent crystals.

Physical properties. Sulphur is a yellow brittle substance, easily crushed into powder. It is available commercially as ground sulphur. The crystal lattice of sulphur is molecular; it is composed of S_8 molecules in the form of puckered rings (Fig. 10.2 *a*). Being a substance with a molecular lattice, sulphur is low-melting: it melts at temperatures only slightly above the boiling point of water to form a very mobile clear yellow liquid. If this liquid is further heated, it becomes brown and loses its mobility. When the vessel is overturned, it flows off very slowly, like resin. When rapidly cooled, overheated sulphur solidifies into a clear brown mass that resembles rubber in its physical properties: when pulled it elongates, and shrinks when released. This allotropic form of sulphur is called plastic sulphur. Its molecules are very long chains of sulphur atoms. When at rest, the chain molecules are arranged at random but when sulphur is stretched the chains straighten in lines parallel to the direction of the stretching effort. When the effort is released, the chains coil back, just like the coils of a spring.

Crystalline and plastic sulphur are allotropic forms of sulphur with different composition, molecular structure, and properties.

When heated strongly, sulphur is converted into a brown vapour.

Sulphur is insoluble in water; it is not even wetted by it. If a pinch of ground sulphur is dropped into water, the particles will not sink but spread on the surface to form a yellow film. This phenomenon is known as *flotation.*

Many naturally occurring metal compounds of sulphur are not wettable either, while the gangue (the material which occurs together with the minerals but is itself of no value) is wettable and sinks to the bottom. Flotation is widely used for separation and concentration of metal ores.

Chemical properties. Since sulphur is a nonmetal, let us first study its reactions with metals. We already know that a mixture of ground sulphur and iron starts reacting when heated at one of its points. The reaction then continues spontaneously at the expense of heat that is liberated in this exothermic reaction. The resultant product is iron sulphide:

$$\overbrace{\mathrm{Fe} + \mathrm{S}}^{2e^-} = \mathrm{Fe}^{+2}\mathrm{S}^{-2}$$

A mixture of powdered aluminium or zinc with sulphur gives a bright flash when ignited. The products of these reactions are white powders of aluminium sulphide or zinc sulphide

$$2\overbrace{\mathrm{Al} + 3\mathrm{S}}^{6e^-} = \mathrm{Al}_2^{+3}\mathrm{S}_3^{-2}$$

$$\overbrace{\mathrm{Zn} + \mathrm{S}}^{2e^-} = \mathrm{Zn}^{+2}\mathrm{S}^{-2}$$

Some reaction products become suspended in air to form a white cloud.

A coil of copper wire burns in sulphur vapour (Fig. 10.3) to form copper(I) sulphide:

$$2\overbrace{\mathrm{Cu} + \mathrm{S}}^{2e^-} = \mathrm{Cu}_2^{+1}\mathrm{S}^{-2}$$

Sulphur reacts with some metals at room temperature. When, for example, liquid mercury is triturated in a mortar with powdered sulphur, mercury sulphide HgS is formed.

Compounds in which sulphur is electronegative are called sulphides.

Sulphur reacts also with hydrogen. As hydrogen is passed into a test tube where molten sulphur is boiling (Fig. 10.4) the odour of rotten eggs can be smelt at the gas-outlet tube. This is the specific odour of hydrogen sulphide, the gaseous compound of sulphur with hydrogen. The reaction equation is as

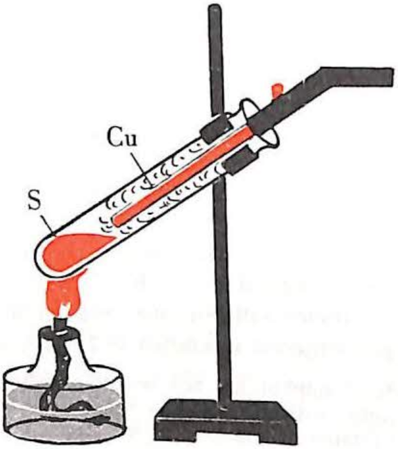

Fig. 10.3 Burning copper in sulphur vapour

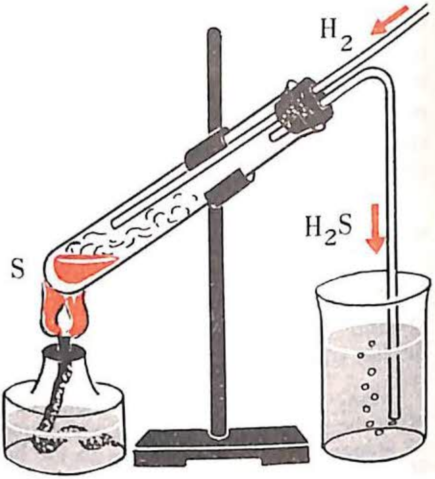

Fig. 10.4 Synthesizing hydrogen sulphide

follows:

$$\overbrace{S + H_2}^{2e^-} = H_2^{+1}S^{-2}$$

Like oxygen, sulphur has the oxidation number of 2 – in its compounds with hydrogen and metals. The composition of hydrogen sulphide is therefore similar to that of water, while the composition of sulphides is like that of metal oxides:

$$H_2^{1+}O^{2-} \quad Na_2^{1+}O^{2-} \quad Zn^{2+}O^{2-} \quad Al_2^{3+}O_3^{2-}$$
$$H_2^{1+}S^{2-} \quad Na_2^{1+}S^{2-} \quad Zn^{2+}S^{2-} \quad Al_2^{3+}S_3^{2-}$$

Let us now consider the reaction of sulphur with oxygen. It acts in this reaction as a reductant. The bonds between sulphur and oxygen atoms are polar; sulphur exhibits its positive, and oxygen of negative oxidation number. Four of all six valency electrons of sulphur may be involved in the formation of bonds. In the former case the reaction product is SO_2 and in the latter, SO_3.

Sulphur readily combines with oxygen to burn in air with a blue flame (in oxygen a dark blue flame). The specific odour of sulphur dioxide SO_2 can be smelt. The gas is colourless. The reaction equation is

$$\overbrace{S + O_2}^{4e^-} = S^{+4}O_2^{-2}$$

? △

1. Describe the physical and chemical properties of sulphur.
2. By what three methods can native sulphur be separated from gangue (from sand for example)?
3. Write down equations for the reactions of sulphur with (a) sodium, and (b) magnesium. Name the reaction products.

10.3 Uses of Sulphur. Sulphur in Nature

Sulphur is used in agriculture to control pests. Leaves of cotton and vine are dusted with powdered sulphur. When sulphur is added to latex and the mixture is heated, a very important product, rubber, is obtained. Rubber is used in the manufacture of a great variety of goods, such as tyres, hoses, tubes, etc. Sulphides form part of the compound of which match heads are made. When a match is lit, we notice the specific odour of sulphur dioxide. Free sulphur is used as a part of gun powder. Large quantities of sulphur are used in the manufacture of sulphuric acid. Like oxygen, sulphur occurs in nature as a simple substance and as its compounds with other elements. Deposits of free sulphur in the Soviet Union are found in Central Asia, the lower Volga areas, and West Ukraine.

Compounds of sulphur are however more abundant. These are sulphur compounds with various metals. Iron pyrite FeS_2, and zinc sulphide ZnS are among them. Sulphur occurs in nature in the form of salts of sulphuric acid, mainly as gypsum $CaSO_4 \cdot 2H_2O$ and sodium sulphate Na_2SO_4. Sulphur is contained in coals as deposits of pyrite. Sulphur is one of the elements which are indispensable for living organisms (sulphur is a part of proteins). Plants take sulphur from the soil.

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1. What are the practical uses of sulphur?
2. In what form does sulphur occur in nature?

10.4 Hydrogen Sulphide

Like all nonmetals, sulphur forms a volatile compound with hydrogen. This is hydrogen sulphide H_2S. The electron-dot formula of this compound is $\mathrm{H}:\overset{..}{\underset{..}{\mathrm{S}}}:\mathrm{H}$ and the structural formula, H—S—H. As in sulphur oxides, the bond with hydrogen is realized in hydrogen sulphide through electron pairs. The bond is thus covalent. But in sulphur oxides these pairs are displaced from the sulphur atoms towards the atoms of oxygen, while in hydrogen sulphide the electrons are displaced from the hydrogen atoms towards the atom of sulphur, i.e. sulphur exhibits its negative oxidation number of 2− in latter compound.

Physical Properties. Hydrogen sulphide is a colourless gas with the smell of rotten eggs. It would actually be more correct to say the reverse: rotten eggs smell of hydrogen sulphide because this gas is always formed during the decay of proteins and is the source of the offensive odour. This odour is a danger sign, because hydrogen sulphide is poison. It destroys the haemoglobin in the blood to recover iron from it and to form iron sulphide. Prolonged inhalation of hydrogen sulphide even in small concentrations is dangerous and can be fatal.

Chemical Properties. Hydrogen sulphide is combustible. It burns in air with a blue flame. The odour of sulphur(IV) oxide is smelt during burning,

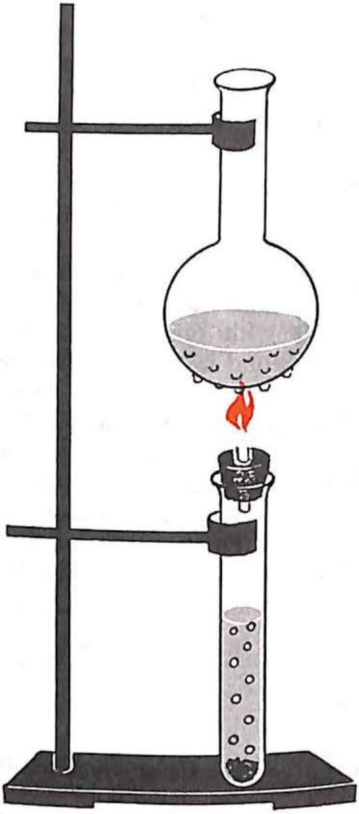


Fig. 10.5 Burning hydrogen sulphide with formation of water

and droplets of water condense on the bottom of a flask (Fig. 10.5):

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

If a cold object is put directly into the flame of a burning hydrogen sulphide, the flame will be cooled, the gas will not burn completely, and sulphur will precipitate on the cold object in the form of a yellow patch:

$$2H_2^{1+}S^{2-} + O_2^0 = 2H_2^{1+}O^{2-} + 2S^0 \downarrow$$

This reaction shows that oxygen can displace sulphur from hydrogen sulphide, i.e. oxygen is more active than sulphur.

Hydrogen sulphide is soluble in water; its aqueous solution is hydrosulphuric acid. It colours litmus red. Salts of hydrosulphuric acid are sulphides. The mentioned iron sulphide FeS is among them. When a lead salt is added to hydrosulphuric acid or to a solution of any sulphide, a black substance precipitates. This is lead sulphide:

$$H_2S + Pb(NO_3)_2 = PbS\downarrow + 2HNO_3$$

$$Na_2S + Pb(NO_3)_2 = PbS\downarrow + 2NaNO_3$$

A salt of lead is a reagent for hydrosulphuric acid and its soluble salts. A paper impregnated in lead salt solution may be used to detect hydrogen sulphide. Blackening of the paper will indicate the presence in the air (or in a solution) of hydrogen sulphide or its soluble salt.

Hydrogen sulphide will normally be prepared in the laboratory by the action of dilute hydrochloric acid on iron sulphide

$$FeS + 2HCl = H_2S\uparrow + FeCl_2$$

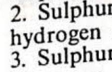
Iron(II) chloride remains in solution while hydrogen sulphide is evolved as a gas. In nature, hydrogen sulphide is formed when organic matter decays. It is contained in the water of some springs in the Caucasus where these waters are used for the therapy of some diseases (baths).

? △

1. Describe the physical and chemical properties of hydrogen sulphide.
2. Sulphur, iron, and hydrochloric acid are provided. Obtain hydrogen sulphide.
3. Sulphur is contained in cast iron in the form of iron sulphide. How can it be detected using a strip of paper impregnated with a solution of a lead salt?
4. Hydrogen sulphide solution becomes cloudy when kept in air. As time passes, it does not colour litmus red. Write the equation for the reaction, bearing in mind that the electronegativities of oxygen and sulphur are different.
5. Blood darkens if hydrogen sulphide enters it. Explain.

10.5 Sulphur Oxides

Sulphur forms two oxides: sulphur dioxide SO_2, which is the oxide of sulphur(IV) and has the structural formula O=S=O; and the oxide of sulphur(VI) SO_3, with the structural formula of



$$\begin{array}{c}O=S=O\\ \|\\ O\end{array}$$

Sulphur(IV) *oxide* SO_2 is a colourless gas with a specific pungent odour. It discolours many organic dyes to form colourless compounds. If a red rose is held in an atmosphere of SO_2, it turns white. Sulphur dioxide discoloures the red solution of fuchsin and the violet ink solution. Blue litmus becomes red in the aqueous solution of sulphur dioxide because sulphurous acid is formed:

$$SO_2 + H_2O = H_2SO_3$$

A solution of sulphurous acid smells of sulphur dioxide because it is evolved from a solution, and if the vessel containing the acid stands open, the acid will be exhausted.

Sulphur dioxide kills microorganisms and it is therefore used to treat fruits and vegetables to prevent their putrefaction in storage. This method is used at canning plants where fruits and vegetables cannot be processed all at once and their prolonged storage is required.

Sulphur(IV) oxide is used to bleach straw, silk, and wool. On the surface of a wet fibre, sulphur dioxide turns into the sulphurous acid which destroys dyes.

In the chemical industry sulphur dioxide is an intermediate product in the manufacture of sulphuric acid.

Sulphur(VI) *oxide* SO_3 is a volatile liquid; it 'fumes' in air. The fume, or more accurately mist, consists of minute droplets of sulphuric acid which is formed as the vapour of sulphur(VI) oxide combines with water vapour contained in the air:

$$SO_3 + H_2O = H_2SO_4 + Q$$

When dissolved in water, sulphur(VI) oxide forms sulphuric acid as well.

Sulphur(VI) oxide is prepared by oxidation of sulphur(IV) oxide in the presence of a catalyst:

$$2S^{4+}O_2^{2-} + O_2^0 = 2S^{6+}O_3^{2-}$$

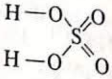
The oxidation number of sulphur changes from 4+ to 6+.

?
Δ

1. What are the physical and chemical properties of sulphur(VI) oxide?
2. A combustible gas that is obtained during coking of coal contains hydrogen sulphide. Why cannot this gas be used as fuel in our houses without preliminary separation from hydrogen sulphide?
3. Describe the properties of sulphur(VI) oxide.

10.6 Sulphuric Acid

The formula of sulphuric acid is H_2SO_4. Its structural formula is



It will be seen from the structural formula that the valency of sulphur is six. The oxidation number of the sulphur atom in sulphuric acid is, as in the oxide SO_3, 6+.

Physical Properties. Sulphuric acid is a heavy colourless liquid (almost twice as heavy as water). It is viscous and oily like vegetable oil. At room temperature it is nonvolatile and therefore has no odour. When sulphuric acid is dissolved in water much heat is liberated due to the formation of stable hydrates of sulphuric acid. If water is added to sulphuric acid, part of the water will not mix with the acid because it is immediately heated to boiling. This causes a splashing of the acid and may seriously damage the skin.

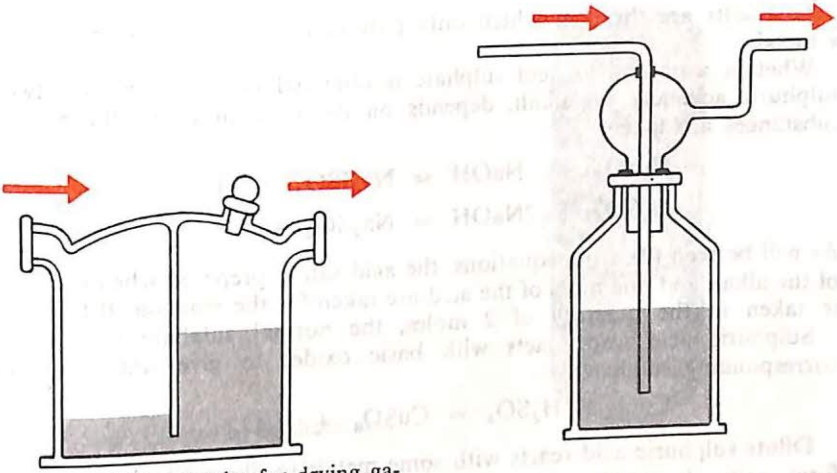


Fig. 10.6 Washing bottles for drying gases

If we place a beaker with sulphuric acid on a balance and weigh it, the beaker will soon become heavier and the balance will be upset. This will happen because concentrated sulphuric acid absorbs moisture from the air. The acid is therefore used to dry substances. Gases, for example, are dried by passing through washing bottles containing concentrated sulphuric acid (Fig. 10.6). When sulphuric acid gets on the skin, it causes severe burns. Special care should be taken when handling concentrated sulphuric acid. In case of accident, sulphuric acid should immediately be removed from the skin or other objects with ample water and the affected site should then be treated with a solution of sodium bicarbonate and washed with water again.

1. What are the physical properties of sulphuric acid?
2. How can sulphuric acid be used to dry (a) liquids and solids, (b) gaseous substances?
3. Cups filled with concentrated sulphuric acid are sometimes placed between frames of windows in cold climates. Explain why. The cups are never completely filled with the sulphuric acid. Explain again.

10.7 Chemical Properties of Sulphuric Acid

One or two hydrogen atoms can be substituted in molecules of sulphuric acid. The acid therefore reacts with the alkali metals to form two series of salts: normal and acid (hydrogen) salts. For example,

Na_2SO_4, K_2SO_4 – these salts are called sulphates (normal salts),

$NaHSO_4$, $KHSO_4$ – these salts are called acid sulphates (or hydrosulphates).

Acid salts are those in which only part of the hydrogen is replaced by a metal.

Whether a normal or acid sulphate is obtained by the reaction between sulphuric acid and an alkali, depends on the ratio in which the reacting substances are taken:

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

As will be seen from the equations, the acid salt is prepared when one mole of the alkali and one mole of the acid are taken for the reaction. If the alkali is taken in the quantity of 2 moles, the normal sulphate is obtained.

Sulphuric acid also reacts with basic oxides to give water and the corresponding sulphate:

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Dilute sulphuric acid reacts with some metals to liberate hydrogen and to form salts. It reacts with metals that come before hydrogen in the electrochemical series. For example:

$$Fe + H_2SO_4 = FeSO_4 + H_2\uparrow$$

Hydrogen atoms contained in sulphuric acid and having the oxidation number of 1+ act as oxidants in this reaction. Dilute sulphuric acid does not act on the metals that come in the electrochemical series after hydrogen (copper, mercury, silver, gold).

The above reactions are common to sulphuric and other acids. But sulphuric acid can enter other reactions that differ it from other acids. When heated, concentrated sulphuric acid reacts with almost all metals irrespective of their position in the electrochemical series. Salts are among the reaction products, but hydrogen is not liberated in these reactions. Concentrated sulphuric acid reacts on heating with copper to form gaseous sulphur(IV) oxide while copper(II) sulphate remains in solution:

$$Cu^0 + 2H_2S^{6+}O_4 = Cu^{2+}SO_4 + 2H_2O + S^{4+}O_2\uparrow$$
$$Cu^0 - 2\bar{e} = Cu^{2+}$$
$$S^{6+} + 2\bar{e} = S^{4+}$$

Concentrated sulphuric acid acts as an oxidant of copper.

Sulphuric acid reacts in a similar way with many other metals. But unlike the dilute acid, concentrated sulphuric acid does not react with iron at room temperature and it can therefore be kept and handled in steel containers. Concentrated and dilute sulphuric acid behave toward metals like two different substances.

A piece of wood placed in concentrated sulphuric acid soon chars. The concentrated acid acts in a similar way on sugar and some other organic substances containing carbon, hydrogen, and oxygen. Sulphuric acid eliminates hydrogen and oxygen from them in the form of water, while carbon is liberated as coal. If ground sugar is mixed with concentrated sul-

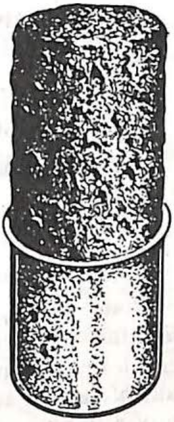


Fig. 10.7 Sugar charred by sulphuric acid

phuric acid into a paste in a beaker, it soon darkens, becomes hot, and a porous carbonaceous mass emerges from the beaker (Fig. 10.7):

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{conc.}}{H_2SO_4} \rightarrow C + \text{hydrates of } H_2SO_4$$

Organic matter is charred by concentrated sulphuric acid due to formation of stable hydrates of sulphuric acid. Being nonvolatile, concentrated sulphuric acid may displace other volatile acids when heated with their salts. When, for example, table salt is heated with concentrated sulphuric acid, hydrogen chloride gas and sodium sulphate are formed:

$$NaCl + H_2SO_4 = HCl\uparrow + NaHSO_4$$
$$2NaCl + H_2SO_4 = 2HCl\uparrow + Na_2SO_4$$

? △

1. Describe the chemical properties of sulphuric acid. Give reaction equations and indicate in which case sulphuric acid acts (a) like an oxidant, (b) like a dehydrating agent, and (c) like a nonvolatile acid.
2*. Divide a solution of sulphuric acid into three equal portions. Neutralize one of them with sodium hydroxide. What salt is formed? Write the reaction equation. Mix the second and the third portions of the acid together and add the same quantity of the alkali as in the former case. What salt is formed? Write the reaction equation. Name its products.
3. Write equations for the reactions (a) between aluminium and dilute sulphuric acid, and (b) between silver and concentrated sulphuric acid when heated.
4. Can sulphuric acid be stored and handled in steel containers? If yes, then under what conditions? Why are steel barrels attacked by corrosion after sulphuric acid is removed from them?

11

Main Regularities of Chemical Reactions. Manufacture of Sulphuric Acid

11.1

Rates of Chemical Reactions

We have studied many reactions and noticed that it takes different time to complete different reactions. Neutralization reactions between acids and alkalis occur practically instantaneously at room temperature and atmospheric pressure. Meanwhile it takes many days for rust to appear on a sheet of steel (rust is the product of the interaction of iron with oxygen and water vapour). Thus, the rates of reactions that may occur under the same conditions of temperature and pressure, may differ significantly.

When carbon, sulphur, or phosphorus burn in air and in pure oxygen, the same reaction products are obtained but the rate of the reaction is much faster in oxygen than in air because the concentration of oxygen in air is only about 0.28 g/litre.

Many examples may be given to illustrate the acceleration of chemical reactions between solids when their particles are reduced in size. For example, reactions of sulphur with iron or zinc with hydrochloric acid, etc.

The rate of a chemical reaction depends on the chemical composition of the reactants and on the conditions of the reaction, namely, concentrations of the reactants, particle size of solid reactants, and on temperature.

It is very important for the chemical science and chemical manufacture that the time during which a given chemical reaction occurs can be calculated.

Consider, by way of illustration, a reaction between hydrogen and iodine vapour with formation of hydrogen iodide:

$$H_2 + I_2 = 2HI$$

It has been found experimentally that the rate of a chemical reaction is proportional to the product of molar concentrations* of the reactants:

$$v = k \cdot C(H_2) \cdot C(I_2)$$

where v is the rate of the reaction, k is the proportionality coefficient called the rate constant of a reaction, and $C(H_2)$ and $C(I_2)$ are molar concentrations of hydrogen and iodine at a given moment.

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* Molar concentration of substances is called the ratio of the quantity of substance in moles to the total volume of solution or other mixture. A unit of molar concentration is one mole per litre (mol/l).

The reaction is carried out in a closed vessel having the capacity of V litres at constant temperature (in a thermostat). Since the number of moles of substances do not change, the pressure inside the vessel should not therefore change either. How do the molar concentrations of the reactants change during the course of the reaction? If, for example, at a certain moment of time t_1 the flask contains n_1 number of moles of hydrogen, and at the moment t_2 this number has changed to n_2 moles of hydrogen, the molar concentrations (in mol/l) of hydrogen C_1 and C_2 are

$$C_1 = \frac{n_1}{V}; \qquad C_2 = \frac{n_2}{V}$$

The average rate of change in the molar concentrations during the course of time $t_2 - t_1$ is (in mol/l·sec)

$$v = \frac{C_1 - C_2}{t_2 - t_1}$$

or

$$v = \frac{\Delta C}{\Delta t}$$

If the given reaction were to occur in the same conditions of temperature and pressure but in a vessel with a doubled capacity, the quantity of hydrogen reacted during given period of time would be two times greater. It means that the rate of reaction does not depend on the capacity of the reaction vessel.

The equation of the reaction rate can now be written as follows:

$$\frac{\Delta C}{\Delta t} = k \cdot C(H_2) \cdot C(I_2)$$

These equations are called *kinetic*. They can be used to calculate the change in concentrations of the reactants during given period of time.

How can the dependence of the reaction rate on the concentration of the reactants be explained? Using the molecular and kinetic theories, it is possible to interpret the mechanism of the interaction of hydrogen with iodine as follows. Molecules of both gases are in constant motion and collide with each other many times. The number of collisions between molecules in the course of one second is very great and if each collision were able to give a hydrogen iodide molecule, the reaction might have been instantaneous. However, it takes considerable time for this reaction to occur which means that only some of the collisions result in the formation of hydrogen iodide molecules. The number of collisions depends on molecular concentrations of the reactants and increases with concentration. The number of collisions is proportional to the product of concentrations, i.e. obeys the same law as the rate of the reaction in question.

10.8 Qualitative Reaction for Sulphuric Acid and Sulphates

The salts of sulphuric acid (except barium sulphate $BaSO_4$, $SrSO_4$, $RaSO_4$, and $PbSO_4$) are soluble in water. If barium chloride solution is added to sulphuric acid or its salt, white barium sulphate precipitates

$$H_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2HCl$$

$$Na_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2NaCl$$

Barium sulphate $BaSO_4$ is insoluble in water or acids. This makes it different from other insoluble salts of barium (e. g. $BaSO_3$) which dissolve in acids with the formation of soluble compounds.

Soluble salts of barium are reagents for sulphuric acid and its soluble salts. If a solution of a barium salt is added to an unknown solution and a white substance (insoluble in nitric acid) precipitates, one can be sure that the unknown solution contains sulphuric acid or its salt.

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1*. A water-soluble salt is used to control pests in agriculture. When (a) silver nitrate or (b) sodium sulphate is added to the solution of this salt a substance precipitates that does not dissolve in water or acids. What is this salt? Write reaction equations.

10.9 Importance of Sulphuric Acid

The chemical industry turns out thousands of chemical products and one of the most important among them is sulphuric acid. Its many valuable properties account for its wide use. First of all sulphuric acid is much cheaper than other acids and it is therefore used in the chemical, metallurgical, petroleum, and many other industries where acids are used (Fig. 10.8). Sulphuric acid is justly called the foundation of chemical industry.

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1. What properties account for the great importance of sulphuric acid in industry? Discuss processes in which sulphuric acid is used in especially large quantities.
2. Fluorine is a component part of natural phosphates. Assume conventionally that fluorine is contained in them as CaF_2 and decide what reaction occurs and why during the action of sulphuric acid on natural phosphates.
3. In the metallurgical industry sulphuric acid is used to clean metal surfaces from their oxides before nickel plating and many other processes. Write equations for the reactions by which ferric sulphate is produced.
4. For what property is sulphuric acid used to dry gases? What is the concentration of sulphuric acid used for the purpose?

Sulphuric acid reacts with many organic compounds. This property of the acid is used to purify pertol and kerosene from harmful impurities. Sulphuric

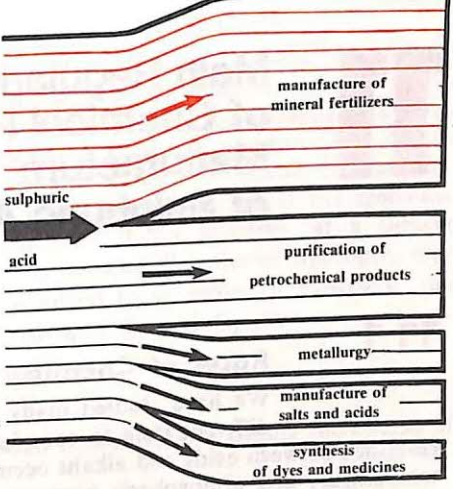

Fig. 10.8 Uses of sulphuric acid. The diagram shows schematically the proportions of the acid used in various industries

acid reacts with these impurities to form compounds that precipitate as insoluble products. Sulphuric acid is widely used in the manufacture of many man-made fibres, detergents, explosives, and dyes.

In the long course of two hundred years that have passed from the moment when sulphuric acid was first produced on a commercial scale its uses invariably changed. The bulk of the acid produced by the chemical industry is ever increasing.

10.10 Oxygen Subgroup

The main subgroup of group VI contains two other elements that are similar to oxygen and especially to sulphur. These are selenium and tellurium. They form gaseous substances with hydrogen: hydrogen selenide H_2Se and hydrogen telluride H_2Te. Like hydrogen sulphide, these compounds are poisons and have an offensive odour. Like the solution of hydrogen sulphide, solutions of hydrogen selenide and hydrogen telluride in water are acids.

Selenious and selenic acids (H_2SeO_3 and H_2SeO_4) and also tellurous acid (H_2TeO_3) are known. They are similar to sulphurous and sulphuric acids in their composition.

Like sulphur, selenium and tellurium have oxidation numbers of 2 −, 4 + and 6 + in their compounds.

The nonmetallic properties of the elements in the oxygen subgroup (like in the subgroup of the halogens) decrease with the increasing atomic number of the elements. Sulphur in the free state does not conduct electricity. Selenium is a poor conductor of electricity while tellurium is a good conductor and it has a metal lustre.

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1. What are common and different properties of the elements and simple substances of (a) oxygen and sulphur, (b) sulphur, selenium and tellurium, and (c) elements in the oxygen subgroup on the one hand, and the halogens on the other hand?

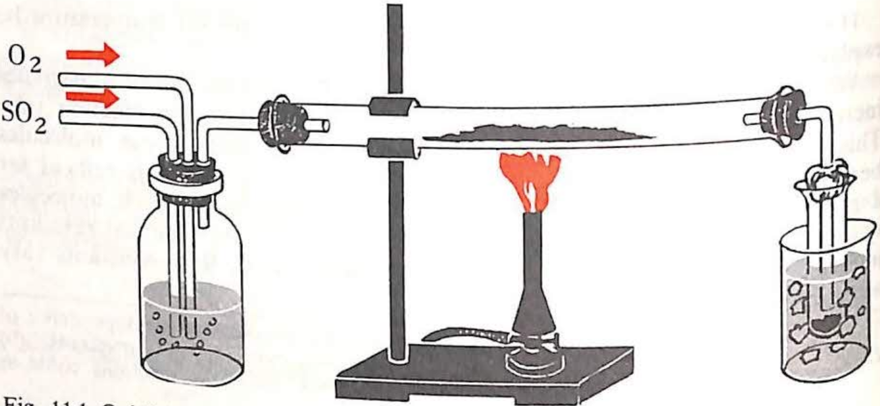

Fig. 11.1 Oxidizing sulphur(IV) oxide over a catalyst

Catalysis is the change of the rate of a chemical reaction in the presence of a catalyst.

Let us become acquainted with some general regularities of catalysis taking the reaction of oxidation of sulphur(IV) oxide with oxygen by way of illustration

$$2SO_2 + O_2 = 2SO_3$$

Pass a mixture of sulphur(IV) oxide and air through a glass tube at a temperature of 20–25°C and then heat the tube over a burner. No reaction occurs. Repeat the experiment but now place a small portion of iron(III) oxide in the tube (Fig. 11.1). No reaction occurs at 20–25°C either, but if we heat the test tube to 500°C the reaction will be initiated. The reaction rate becomes significant if heating is continued to higher temperatures. Sulphur(VI) oxide is collected in the receptacle. The iron(III) oxide has not changed. The reaction is catalytic and iron(III) oxide is a catalyst whose activity becomes effective at temperatures over 500°C.

How can the role of ferric oxide be explained in this reaction? According to some theories the reactants adsorb on the surface of the catalyst (ferric oxide in our case) to form unstable intermediate compounds which then break up to give the final product and to recover the catalyst:

$$A + C = AC$$
$$AC + B = AB + C$$

where A and B are the reactants and C is the catalyst.

Each step in this mechanism is much faster than the direct interaction between the molecules of the reactants.

There are some points in this theory that require further discussion.

Is there only one substance that can act as a catalyst in a given reaction or may some other substance prove as effective? Can one substance be used as a catalyst in several reactions?

Experience shows that many chemical reactions are accelerated by various catalysts. Crushed platinum, ferric oxide and vanadium(V) oxide, the catalysts used in the oxidation of SO_2 to SO_3, can for example catalyze another very important reaction, the oxidation of ammonia to nitrogen(II) oxide.

If a mixture of sulphur(IV) oxide and air that is passed over a catalyst, contains a small quantity of arsenic(V) oxide, the reaction rate will soon decrease and in a certain period of time the reaction will stop completely. This is due to *poisoning* of the catalyst. The substance that sharply decreases the rate of catalytic reactions is called *catalytic poison.* Poison reacts with the catalyst to form compounds whose stability is higher than that of compounds formed by the interaction of the initial reactants with the catalyst. This is how the phenomenon of poisoning can be explained.

Catalysis widely occurs in nature and it performs a very important role in the life of all living organisms. The importance of catalysis in industry is great as well: by using catalysts many important reactions can be carried out in a short period of time. The petrochemical industry especially depends on catalysis.

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△

1. How does the rate of a catalytic reaction depend on molar concentrations of the reacting substances?
2. Formulate regularities of changes in the rate of catalytic reactions with increasing temperature.
3. Do the particle size and porosity of a catalyst matter?

11

Main Regularities of Chemical Reactions. Manufacture of Sulphuric Acid

11.1

Rates of Chemical Reactions

We have studied many reactions and noticed that it takes different time to complete different reactions. Neutralization reactions between acids and alkalis occur practically instantaneously at room temperature and atmospheric pressure. Meanwhile it takes many days for rust to appear on a sheet of steel (rust is the product of the interaction of iron with oxygen and water vapour). Thus, the rates of reactions that may occur under the same conditions of temperature and pressure, may differ significantly.

When carbon, sulphur, or phosphorus burn in air and in pure oxygen, the same reaction products are obtained but the rate of the reaction is much faster in oxygen than in air because the concentration of oxygen in air is only about 0.28 g/litre.

Many examples may be given to illustrate the acceleration of chemical reactions between solids when their particles are reduced in size. For example, reactions of sulphur with iron or zinc with hydrochloric acid, etc.

The rate of a chemical reaction depends on the chemical composition of the reactants and on the conditions of the reaction, namely, concentrations of the reactants, particle size of solid reactants, and on temperature.

It is very important for the chemical science and chemical manufacture that the time during which a given chemical reaction occurs can be calculated.

Consider, by way of illustration, a reaction between hydrogen and iodine vapour with formation of hydrogen iodide:

$$H_2 + I_2 = 2HI$$

It has been found experimentally that the rate of a chemical reaction is proportional to the product of molar concentrations* of the reactants:

$$v = k \cdot C(H_2) \cdot C(I_2)$$

where v is the rate of the reaction, k is the proportionality coefficient called the rate constant of a reaction, and $C(H_2)$ and $C(I_2)$ are molar concentrations of hydrogen and iodine at a given moment.

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* Molar concentration of substances is called the ratio of the quantity of substance in moles to the total volume of solution or other mixture. A unit of molar concentration is one mole per litre (mol/l).

The reaction is carried out in a closed vessel having the capacity of V litres at constant temperature (in a thermostat). Since the number of moles of substances do not change, the pressure inside the vessel should not therefore change either. How do the molar concentrations of the reactants change during the course of the reaction? If, for example, at a certain moment of time t_1 the flask contains n_1 number of moles of hydrogen, and at the moment t_2 this number has changed to n_2 moles of hydrogen, the molar concentrations (in mol/l) of hydrogen C_1 and C_2 are

$$C_1 = \frac{n_1}{V}; \qquad C_2 = \frac{n_2}{V}$$

The average rate of change in the molar concentrations during the course of time $t_2 - t_1$ is (in mol/l·sec)

$$v = \frac{C_1 - C_2}{t_2 - t_1}$$

or

$$v = \frac{\Delta C}{\Delta t}$$

If the given reaction were to occur in the same conditions of temperature and pressure but in a vessel with a doubled capacity, the quantity of hydrogen reacted during given period of time would be two times greater. It means that the rate of reaction does not depend on the capacity of the reaction vessel.

The equation of the reaction rate can now be written as follows:

$$\frac{\Delta C}{\Delta t} = k \cdot C(H_2) \cdot C(I_2)$$

These equations are called *kinetic*. They can be used to calculate the change in concentrations of the reactants during given period of time.

How can the dependence of the reaction rate on the concentration of the reactants be explained? Using the molecular and kinetic theories, it is possible to interpret the mechanism of the interaction of hydrogen with iodine as follows. Molecules of both gases are in constant motion and collide with each other many times. The number of collisions between molecules in the course of one second is very great and if each collision were able to give a hydrogen iodide molecule, the reaction might have been instantaneous. However, it takes considerable time for this reaction to occur which means that only some of the collisions result in the formation of hydrogen iodide molecules. The number of collisions depends on molecular concentrations of the reactants and increases with concentration. The number of collisions is proportional to the product of concentrations, i. e. obeys the same law as the rate of the reaction in question.

Using this information one can formulate a conclusion:

If a reaction occurs as a result of collisions between pairs of molecules, then the reaction rate is proportional to the product of molar concentrations of given substances:

$$v = k \cdot C(\mathrm{A}) \cdot C(\mathrm{B})$$

where v is the reaction rate, k is the rate constant of a given reaction, and $C(\mathrm{A})$ and $C(\mathrm{B})$ are molar concentrations of substances A and B that enter the reaction.

Let us consider the rate of the reaction:

$$H_2 + Cl_2 = 2HCl$$

If your solution of the problem of the reaction rate reads as follows:

$$v = k \cdot C(H_2) \cdot C(Cl_2)$$

you have made a mistake.

Remember that this reaction (see section 9.2) is a chain reaction and the growth of the chain includes two stages

$$Cl + H_2 = HCl + H \qquad (1)$$

$$H + Cl_2 = HCl + Cl \qquad (2)$$

Using these data, one can make out a kinetic equation for each stage. According to the general regularity (proportionality to the product of molar concentrations of the reactants), these equations are as follows

$$v_1 = k \cdot C(Cl) \cdot C(H_2); \qquad v_2 = k_2 \cdot C(H) \cdot C(Cl_2)$$

It is evident that kinetic equations may not be derived from chemical equations, since the latter only indicate which substances enter the reaction and in what quantities, and which substances are formed, but they give no indication of the mechanism of the reaction.

Why does the rate of a chemical reaction increase with the decreasing particle size of solid reactants?

Consider a reaction, for example, between a gas and a solid. The molecules of the gas collide with the surface of the solid. The greater the number of such collisions per unit time, the higher the reaction rate. The number of collisions increases with increasing concentration of the gas and the surface area of the solid. This regularity holds for all reactions between substances in different states of aggregation: between gas and solid, between gas and liquid, between liquid and solid, between two solids, and between immiscible liquids. These reactions are called *heterogeneous* in contrast to *homogeneous* reactions that occur between gases or two miscible liquids. *The rate of a heterogeneous reaction is proportional to the surface area over which the reacting substances contact each other.*

How does the rate of a reaction depend on temperature? Consider the experimentally found data on the formation of water from a mixture of hydrogen and oxygen. At room temperature the reaction will not occur, hence the reaction rate is zero. At 400 °C it is completed in 80 days, at 500 °C in two hours, and at 600 °C the reaction occurs instantaneously with an explosion.

How can this strong dependence of the reaction rate on temperature be explained?

When temperature increases, the number of collisions between particles increases too but this increase is several times less than the reaction rate. This indicates that there must be another cause. Only those molecules become reactive whose energy acquires a certain value which is critical for a given reaction. As temperature increases the number of such molecules increases too. According to average data, the rate of most chemical reactions increases 2–4 times as the temperature rises some 10 °C. Rate constants vary accordingly.

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1. What known reactions will you use to illustrate the dependence of the reaction rate on: (a) concentration of the reactants, (b) temperature, and (c) surface area over which the reactants come in contact?
2. Why is the reaction carried out at constant temperature during experimental determination of the rate of the reaction between hydrogen and iodine? Why does the pressure inside the reaction vessel remain constant?
3. The rate of the reaction between hydrogen and iodine was estimated by the change in concentration of hydrogen. What is the average rate of change in molar concentrations of iodine and hydrogen iodide during the same period of time?
4. Calculate the average rate of the reaction between carbon(II) oxide and gaseous chlorine by which phosgene $COCl_2$ is formed ($CO + Cl_2 = COCl_2$), if the initial molar concentration of chlorine or carbon monoxide was 0.01873 mol/l and in 12 minutes it was 0.01794 mol/l.
5. How does the reaction rate increase if the temperature increases from 200 to 300 °C and a rise of 10 °C causes the reaction rate to double?
6. How do the rate constants of most reactions change with increasing temperature?
7. Compare three cases of a reaction between gaseous substances $A + B = 2C$ if the reaction rate is expressed by the equation $v = k \cdot C(A) \cdot C(B)$. In the first case the initial molar concentration of each gas was 0.01 mol/l. In the second case the molar concentration of substance A was 0.04 mol/l, while that of substance B remained 0.01 mol/l. In the third case the initial concentration of each substance was 0.04 mol/l. How do the numbers of collisions between molecules per unit time compare in these three cases?

11.2 Catalysis

We studied earlier the methods of manufacture of oxygen and found out that the rate of decomposition of hydrogen peroxide increases markedly if a small quantity of manganese(IV) oxide is added. Manganese(IV) oxide is not spent in the reaction. It is a catalyst.

Catalysts are substances that are used in chemical reactions to alter their rates without themselves changing by the end of the reaction. Reactions whose rates can be altered by catalysts are called catalytic reactions.

11.3 Chemical Equilibrium

Many chemical reactions may proceed in both a forward and reverse direction: for example, the reaction of decomposition of mercury oxide into mercury and oxygen, and formation of mercury oxide from mercury and oxygen; or the reactions of formation and decomposition of water; formation and decomposition of sulphurous acid, etc.

Consider the reaction of oxidation of sulphur dioxide from this standpoint

$$2SO_2 + O_2 = 2SO_3 + Q$$

If sulphur(VI) oxide is passed over the same catalyst that was used to oxidize sulphur(IV) oxide and the same temperature is maintained, we find that sulphur(VI) oxide is partly decomposed into sulphur(IV) oxide and oxygen:

$$2SO_3 = 2SO_2 + O_2 - Q$$

One of these two reactions, for example oxidation of SO_2 to SO_3, may be called forward (direct) and the other, a reverse reaction.

It is unnecessary to write both equations to express the essence of these two reactions. They can be united in one equation by placing two arrows pointing in opposite directions between them instead of the equality sign:

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

Chemical reactions which occur simultaneously in opposite directions under the same conditions are called reversible reactions.

In accordance with general regularities, rates of forward and reverse reactions increase with increasing temperature. But it should be pointed out that: at 400°C 99.2 per cent of sulphur(IV) oxide is oxidized, at 500°C 93.5 per cent, at 600°C 73.0 per cent, and at 1000°C only 5 per cent. No matter how long we keep the reactants at a given temperature, unreacted sulphur(IV) oxide remains in the mixture. The reverse reaction is not completed either: non-decomposed SO_3 remains in the mixture in a quantity equal to that which is formed (under the same conditions) from sulphur dioxide SO_2 and oxygen.

A question arises: why do reversible reactions not proceed to the end but instead attain a certain threshold after which the reaction seems to be suspended? To answer this question let us consider the change in the rates of forward and reverse reactions between sulphur dioxide and oxygen under constant temperature and pressure.

Molar concentrations of sulphur dioxide and oxygen in the gaseous mixture gradually decrease and the rate of forward reaction v_{for} (oxidation of SO_2 to SO_3) decreases accordingly. The molar concentration of sulphur(VI) oxide in the formed gaseous mixture gradually increases and hence the rate of the reverse reaction v_{rev} increases. After a certain period of time the two reaction rates will certainly be equal

$$v_{for} = v_{rev}$$

Both forward and reverse reactions continue but the composition of the mixture remains constant due to equality of the rates of both reactions. **The state of a reacting mixture at the moment when the number of molecules of substances formed is equal to the number of molecules entered in the reaction is called the state of chemical equilibrium.**

The composition of a mixture at the state of equilibrium is called *equilibrium composition*. It should be noted that the state of equilibrium is established not because the reactions have finished but because the forward and reverse reactions occur simultaneously in opposite directions. This equilibrium is called *dynamic*.

The above data on the maximum degree of oxidation of sulphur(IV) oxide characterize the equilibrium composition of the mixture at various temperatures. As temperature increases the concentration of sulphur(VI) oxide in this mixture decreases. Why?

As the temperature of the forward and reverse reactions increases, the rates of these reactions change in a different way: the rate of decomposition of sulphur(VI) oxide increases faster than the rate of the forward reaction. It should be pointed out that the forward reaction is exothermic while the reverse is endothermic.

In this particular case the following general regularity, characterizing the dependence of equilibrium on temperature, holds: *as the temperature increases, equilibrium of an exothermic reaction is shifted towards the formation of the initial substances, while equilibrium of an endothermic reaction is shifted towards the formation of the reaction products.*

How does the presence of a catalyst affect equilibrium? The answer can be found by carrying out reactions with different catalysts. It has been found experimentally that whatever catalyst might be used, the same portion of sulphur(IV) oxide is oxidized under the same conditions. This is the general regularity.

A catalyst accelerates both the forward and the reverse reactions without affecting the state of equilibrium. Dynamic equilibrium can be established in physical processes as well. For example, if a closed vessel contains a certain amount of water at constant temperature, the state of equilibrium between water and water vapour in the space above the water surface will soon be attained, because the number of water molecules evaporated during a certain time is equal to the number of vapour molecules that are condensed back to water.

The concepts of chemical equilibrium and reaction rate are very important for the science of chemistry and for the chemical industry. Once data on chemical equilibrium are available, it is possible to calculate the equilibrium (maximum) yield of the desired product depending on molar concentrations of the reacting substances, pressure, and temperature.

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Δ

1. In what direction will the following equilibria shift with increasing temperature?

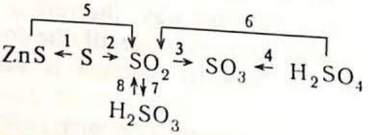
$2H_2 + O_2 \rightleftarrows 2H_2O + Q \qquad SO_2 + H_2O \rightleftarrows H_2SO_3 + Q$

$CaCO_3 \rightleftarrows CaO + CO_2 - Q \qquad CO + H_2O \rightleftarrows CO_2 + H_2 + Q$

2. A system of sulphur(IV) oxide, oxygen, and sulphur(VI) oxide at chemical equilibrium is given. During an interval of time of 1 second, n molecules of sulphur(VI) oxide are formed. What number of oxygen molecules are formed during this time?

3. Consider the process of dissolution of a solid in liquid to the point where chemical equilibrium is attained. Do dissolution and crystallization processes occur in this system at the state of equilibrium? How can this equilibrium be shifted toward crystallization?

4. Write equations for reactions between substances in the directions indicated by the arrows in the diagram below. Specify conditions necessary to accomplish these reactions.



11.4 Manufacture of Sulphuric Acid. Raw Materials for the Manufacture of Sulphuric Acid

Sulphur is one of the most abundant elements in the Earth's crust. It occurs as free sulphur, as metal sulphides, various sulphates, and other compounds. Sulphur compounds are contained in all natural fuels.

Rich deposits of native sulphur, iron pyrite FeS_2, and calcium sulphate are known. All these raw materials are used in the manufacture of sulphuric acid. But there are still some other substances that are used for the purpose. Many nonferrous metals, e.g. copper, zinc, lead and others, are obtained from natural sulphides. The first step in the manufacture of these metals is roasting in a stream of air. The resultant gas contains sulphur(IV) oxide. Formerly this gas was discharged into the atmosphere and caused serious damage to the environment. At the present time this gas is used to prepare sulphuric acid.

In addition to copper sulphides, copper ores also contain iron pyrite FeS_2. These ores are separated into a concentrate, containing a relatively large amount of copper, and wastes containing pyrite. The wastes are first crushed and pyrite is then used in the manufacture of sulphuric acid.

Large quantities of natural fuel are burnt at power stations, industrial, and other furnaces. If you now smell the smoke gas you will notice the odour of sulphur dioxide which is contained in this waste gas. But it is difficult to recover sulphur dioxide from smoke and use it in the manufacture of sulphuric acid because its concentration in the gas is very low. Many researchers are working on the problem of recovery and utilization of this gas.

When coal is heated without the access of air to produce coke, coke gas containing hydrogen sulphide is formed. Sulphur or sulphur(IV) oxide are produced from it at coke plants.

Many natural gases contain considerable amounts of hydrogen sulphide from which the gas should be purified. This is another raw material for the production of sulphuric acid.

So in addition to naturally occurring materials that may be used to prepare sulphuric acid, the wastes of other industries should also be used for the same purpose. Two objectives are thus attained: the environment is protected from pollution, and the cost of producing sulphuric acid is cut. The utilization of natural resources that makes use of all the components of raw materials is called *complex utilization*.

?
△

1. Why are sulphides an indispensable part of all natural fuels?
2. By what reactions can sulphuric acid be prepared from: (a) sulphur, (b) pyrite, (c) hydrogen sulphide, (d) the waste gas of copper smelting plants?
3. In 1958 about 71 per cent of sulphuric acid was prepared in the Soviet Union from pyrite (wastes of copper production included). In 1970 the overall Soviet production of sulphuric acid increased considerably while the percentage of the acid produced from pyrite decreased to 41.8%. What conclusion can be derived concerning the raw materials used for the manufacture of sulphuric acid?
4. Draw a diagram of the complex processing of copper ores.

11.5 Preparing Sulphur(IV) Oxide (the First Step in the Manufacture of Sulphuric Acid)

If you answered question 2 (to the previous section) correctly you know that the first stage in the manufacture of sulphuric acid from sulphur, pyrite and hydrogen sulphide is their combustion to prepare the gas containing sulphur(IV) oxide. It is easy to imagine that combustion of hydrogen sulphide, molten sulphur, or pyrite is similar to the burning of fuels, heavy fractions of petroleum, or of coal in a furnace. Consider in detail the roasting of pyrite:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 + Q$$

Obviously the reaction should be carried out in conditions under which the sulphur contained in pyrite can be utilized as completely as possible to prepare sulphur(IV) oxide and the reaction can be carried out at the fastest rate possible. The productive capacity of the furnace, i. e. the weight of pyrite burnt in it during a day, increases with the increasing rate of roasting.

In order to choose the optimum conditions it is necessary to know the physicochemical conditions of the process, the conditions of chemical equilibrium and reaction rates. The oxidation of pyrite is irreversible. Its rate increases with increasing the concentration of oxygen, the temperature, and

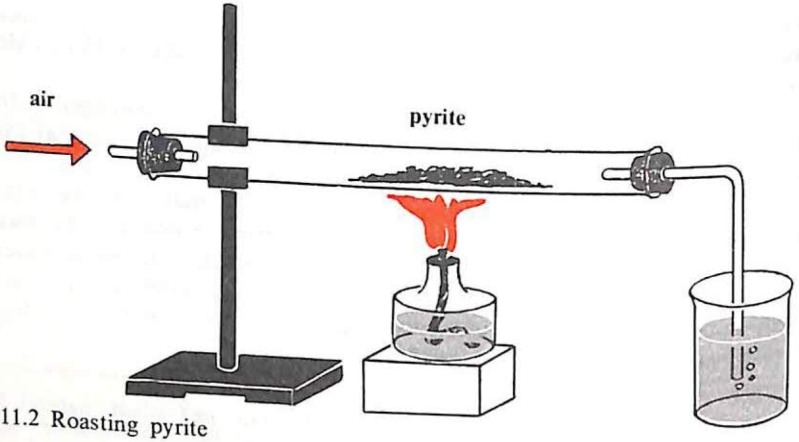


Fig. 11.2 Roasting pyrite

the surface area over which oxygen and pyrite come in contact (i.e. with decreasing particle size of pyrite).

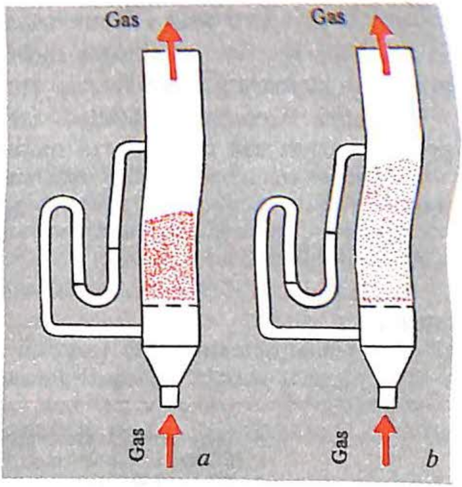
In order to specify the conditions for the reaction, carry out an experiment using the apparatus shown in Fig. 11.2. Pass air over a bed of pyrite in the tube at room temperature: no reaction occurs. The reaction becomes appreciable only at temperatures of 400°C and is accelerated at higher temperatures. Without stopping the delivery of air, put aside the burner: the reaction continues spontaneously, which means that it is exothermic. When the reaction is over, examine the tube contents: the yellow substance must be ferric oxide Fe_2O_3. Use an indicator to prove that sulphur(IV) oxide has formed (the indicator colour changes); the odour is another indication of the presence of sulphur dioxide.

Now repeat the experiment using oxygen instead of air: the reaction is accelerated. The reaction can also be accelerated by decreasing the particle size of pyrite. But as the bed of the solid becomes more compact, it becomes difficult to pass air or oxygen through it. Consider this phenomenon in more detail. Carry out an experiment in an apparatus shown in Fig. 11.3. Place a bed of fine sand over a sieve. Now supply air. The pressure should be rather high if we want the air to pass through the bed of sand, but the stream of air will entrap particles of sand and carry them away. If however the pressure is slightly reduced, the sand particles will not be carried by the air but the bed of sand will become loose. This is known as *fluidized bed* to indicate that the bed of sand resembles in certain aspects a boiling liquid.

Will the rate of the reaction increase in a fluidized bed? One can justly suggest that it will, because the surface over which the reactants make contact with each other increases. Each particle is washed with gas inside the fluidized bed and a uniform temperature is maintained throughout the bed due to constant stirring of the loose material by the gas.

What are the *optimum conditions* for roasting pyrite in industry? What is

Fig. 11.3 The same amount of solid is placed in a column but gas is blown through it at (*a*) low and (*b*) high flow rates. A fluidized bed is formed in the latter case



the required oxygen content of the blown-in gas? What is the particle size of pyrite? What is the roasting temperature?

Replacement of air by oxygen intensifies the reaction but oxygen is not yet used everywhere because of its relatively high cost. Air is therefore also used.

The discovery of the phenomenon of a fluidized bed made it possible to intensify many reactions between solid and gaseous substances. Roasting in a furnace with a fluidized bed continues for a few seconds while formerly this process took hours. Hence the advantage of using fluidized-bed furnaces. The process in such a furnace is of course continuous and completely automatic (see plate IV on page 229). Pyrite is loaded into the hopper by a belt conveyer. From the hopper pyrite is fed continually into the furnace and a continuous flow of air is blown through pipes into the furnace from below. The cinder (roasted material) is partly carried with flue gas and is partly withdrawn from the furnace through a special opening in the side wall of the furnace.

One might justly expect that the temperature would be as high as possible but it is actually maintained at 800°C because at higher temperatures solid particles sinter together to form larger aggregations. The temperature is controlled by carrying out the reaction with rather more air than theory suggests. Moreover, tubes of a steam boiler are placed inside the furnace so that the heat liberated during the process might be utilized. Steam generated in the boiler is used to produce electricity and for other purposes.

What is the optimum capacity of a furnace, i. e. what weight of pyrite may conveniently be roasted in it?

When large furnaces are constructed, their costs per unit product decrease and the efficiency of labour increases. The capacity of furnaces used in modern industry is about 300 000 tons of sulphuric acid a year (calculating with reference to 100 per cent sulphuric acid).

Modern powerful furnaces cannot be controlled manually and they are therefore provided with various instruments and automatic regulators which control the reaction conditions such as the temperature inside the reaction zone (by increasing air delivery), etc.

We have become acquainted with roasting of pyrite and with some principles that are common to many chemical industrial processes:

in order to increase the efficiency of reaction apparatuses, chemical reactions are carried out at the highest possible rates;

reactions between solid and gaseous materials should preferably be carried out in fluidized-bed reactors;

heat produced during the reaction should be utilized, e. g. for generation of steam;

it is reasonable to build reaction apparatuses of high capacity;

the process should be continuous and fully automated.

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1. Why should sintering of particles during roasting of pyrite in a fluidized-bed furnace be prevented?

△ 2. What methods do you know by which the rate of the reaction between solid and gaseous substances can be intensified?

3. A partial loss of sulphur with roast wastes is considered inevitable. Explain why we have to put up with this disadvantage. (Use the data on the reaction rate to explain your answer.)

4. In optimum conditions about 98 per cent of sulphur is only converted into sulphur dioxide SO_2. What amount of sulphur(IV) oxide can be obtained by roasting one ton of pyrite containing 45 per cent of sulphur?

5. A roasting furnace works continuously. A laboratory plant in which the described experiment can be carried out is a batch unit. What are the advantages of the continuous process over a batch process?

6. What quantity of pyrite can be roasted during one day in a furnace (the capacity of which is indicated in the text) if 5 per cent of sulphur contained in the pyrite is lost? The furnace is run continuously throughout the year.

11.6 Optimum Conditions for Oxidation of Sulphur(IV) Oxide

Sulphur(IV) oxide should be oxidized to sulphur(VI) oxide:

$$2SO_2 + O_2 = 2SO_3 + Q$$

This reaction is reversible. As has already been said, a maximum 99.2 per cent of sulphur(IV) oxide can be oxidized under atmospheric pressure with a slight excess of oxygen at 400°C and only 73 per cent at 600°C. Catalysts are known which speed up oxidation of sulphur(IV) oxide. These are platinum, iron and vanadium oxides. Are these catalysts equally effective? The reaction becomes noticeable at about 350°C with platinum, at about 400°C with vanadium, and at about 550°C with the iron catalyst. Platinum is thus the most active catalyst for oxidation of sulphur dioxide, ferric oxide Fe_2O_3 is the least active, and the vanadium catalyst occupies the intermediate position.

The rate of catalytic reactions increases with temperature but if the temperature is raised above a certain limit (specific for each particular solid catalyst) the reaction rate sharply decreases. This critical temperature is 620°C for the vanadium catalyst. At this temperature, processes are probably initiated in the catalyst which change its structure and even chemical composition. These changes occur in optimum conditions as well but they become appreciable only after a certain period of time (sometimes a long period). The platinum catalysts remain effective for 10-15 years and then the conversion of sulphur dioxide into sulphur(VI) oxide becomes less effective; this term is only about 5 years for the vanadium catalyst.

The gas produced during pyrite roasting contains various impurities. Arsenic(III) oxide is among them. These impurities poison catalysts.

The considered reaction occurs between two gases; the reaction product is gas too, but a solid catalyst is involved and the reaction is therefore heterogeneous. All regularities that we observed in pyrite roasting hold for this heterogeneous reaction.

Consider now the problem of optimum industrial conditions for oxidation of sulphur(IV) oxide.

Which catalyst is to be preferred? Of course the most effective catalyst is platinum and it was earlier used for the purpose, but it is very expensive. The search for a cheaper but effective catalyst resulted in the discovery of catalytic properties in vanadium(V) oxide which is now used in the manufacture of sulphuric acid.

In order to ensure complete oxidation of SO_2 to SO_3, the reaction should be discontinued at about 400-450°C. But the reaction rate at this temperature is low. In order to attain the maximum possible rate, the reaction should be begun at the maximum permissible temperature (about 600°C) and then, as the concentration of SO_3 increases, the temperature should be gradually lowered to 400-450°C.

Below follows a brief description of the optimum process for oxidation of sulphur(IV) oxide. When pyrite is burnt, a gaseous mixture is produced, which contains various dusts and poisons. (When sulphur dioxide is prepared by burning sulphur and hydrogen sulphide, the gas mixtures are much purer; this simplifies the process of manufacture of sulphuric acid.) Gaseous mixtures are separated from dust by a very important industrial procedure. Let us acquaint ourselves with the operating principle of the apparatuses used for separation of dusts in the industrial manufacture of sulphuric acid. These apparatuses are cyclones and electric filters.

In a cyclone dust particles are separated from the gas mixture by centrifugal force. A cyclone (see colour plate IV) consists of two cylinders placed one inside the other. Gas is delivered into the larger cylinder in its upper portion and is forced downward in spiral motion. Under the effect of the centrifugal force solid particles are thrown toward the wall of the outer cylinder and precipitate in the conical part of the apparatus, from which they are removed. Thus cleaned gas is discharged from the cyclone through the inner cylinder. This is a simple but a very effective separating apparatus. But it fails to separate very fine dust particles from gas and further purification is therefore necessary. Electric filters (the same colour plate IV) are used for final purification of gas. Under the action of a strong electric field, the molecules of the gaseous substance are ionized. Dust particles collide with the ions and become charged as well, and then are attracted to one of the electrodes upon which they are discharged and precipitated. When the electrodes are shaken dust particles fall off and are removed from the apparatus.

The gas separated from dust is then dried. To do this it is brought into contact with concentrated sulphuric acid. This is a heterogeneous process and its rate increases with increasing the surface of contact between gas and liquid. Just imagine a drying column packed with rings (ceramic or metal) into which sulphuric acid is delivered from the top (see the same colour plate). As the acid flows down, it forms films on the surface of the rings. The gas to be dried is delivered from the bottom. The surface area over which gas and liquid come into contact is very great in such a column. Gas and liquid move in countercurrent streams which is necessary to ensure a high degree of drying. When gas leaves the column, it contains small amounts of moisture, but in the upper portion of the column partly dried gas comes into contact with fresh portions of concentrated sulphuric acid which avidly absorbs the remaining moisture. This ensures high efficiency of gas drying.

The purified gas should be heated to the temperature at which the reaction begins. Can the heat liberated during oxidation of sulphur(IV) oxide be utilized to preheat the gas? Of course it would be quite reasonable to do that. A special heat exchanger (plate IV) is used for the purpose. The dried gas is preheated before it enters the catalyst chamber. The design of the heat exchanger is simple. Normaly shell-and-tube type apparatuses are used. These are cylinders inside which tubes are arranged. Hot gas is passed through the tubes while the gas to be preheated is passed in a countercurrent stream in the space between the tubes.

In order to increase the surface area across which gas comes into contact with the catalyst, the solid catalyst is crushed. If the catalyst is reduced to very fine particles, the process can be carried out in the fluidized bed. Apparatuses with fluidized beds are now used in industry but apparatuses with stationary catalyst placed over grates, are also widely used.

In the catalyst chamber shown in plate IV there are several beds of catalyst. Heat exchangers, by which the temperature of the catalyst is controlled, are placed between the catalyst beds. The capacities of modern catalyst chambers correspond to the capacities of newly erected furnaces. One contact apparatus can thus handle the entire bulk of the gas produced in the furnace. About 99 per cent of sulphur(IV) oxide is converted into sulphur(VI) oxide.

In the study of this process we became acquainted with the principles formulated in the previous section. At the same time we got acquainted with some new principles that are also widely used in chemical and other industries:

1. In a reversible exothermic reaction (in contrast to an irreversible reaction) the optimum temperature conditions are characterized by a gradual fall in the course of the reaction.

2. The general requirements for the industrial catalysts are the following: activity, stability, long life, relatively low cost, and resistance to poisoning. In turn the reactants should not contain substances that might poison or otherwise contaminate the catalyst.

3. Reactants are passed in countercurrent flows.

4. Heat is exchanged between the flows of substances involved (to control temperature and to utilize the heat of reaction).

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1. In what cases is the oxidation of sulphur(IV) oxide not the second but the first stage in the manufacture of sulphuric acid?
2. Why should pyrite be roasted at a constant temperature (e.g. at 800°C), while sulphur(IV) oxide should be oxidized at variable temperatures?
3. Ferric oxide Fe_2O_3 is a cheap and durable catalyst but it is not used for the industrial manufacture of sulphuric acid. Explain why.
4. Why should the gaseous mixture be purified thoroughly from dust before it is delivered to the catalyst chamber for oxidation even if the dust does not contain any poisons? Explain.
5. Why should the gas be dried?
6. Once we know the properties of concentrated sulphuric acid and principles of chemical kinetics, substantiate the design of a drying column.
7. Why should the depth of catalyst beds be increased as the gas passes farther into the apparatus?
8. Why is sulphur(IV) oxide not oxidized completely?

11.7 Final Stage of Manufacture of Sulphuric Acid

Sulphur(VI) oxide formed in the catalyst chamber should be separated from the gaseous mixture in which its content is 7 per cent by volume. This is necessary to produce concentrated sulphuric acid or a solution of SO_3 in sulphuric acid (oleum).

Sulphuric acid is produced from sulphur(VI) oxide:

$$SO_3 + H_2O = H_2SO_4 + Q$$

This reaction is irreversible at temperatures under 300°C. The reaction occurs during a short period of time. The rate of the reaction increases with the increasing of surface area over which gas and liquid contact each other.

At first sight it seems that it is not difficult to choose optimum conditions for the reaction. The reaction should be carried out at moderate temperatures, in a column packed with rings, and with countercurrent flows of the gaseous mixture and the liquid that absorbs sulphur(VI) oxide. But in practice one should remember that sulphur(VI) oxide reacts very rapidly with water vapour with instantaneous formation of sulphuric acid vapour. The gaseous mixture thus becomes oversaturated with vapour of sulphuric acid.

You already know what happens when moist air is quickly cooled: mist is formed which becomes suspended in the atmosphere for a long time. The same happens to sulphuric acid vapour, but even more so because sulphuric acid is condensed at a rather high temperature. This mist cannot be absorbed completely by the liquid in the absorbing towers and is thus discharged into the atmosphere to poison the environment unless it is trapped in special devices. But maybe it is possible to carry out a reaction between sulphur(VI) oxide and water to prevent the formation of the mist?

Yes, it is possible to do so and it is necessary to absorb sulphur(VI) oxide by sulphuric acid in which the water content is as low as 2 per cent (by weight). The water vapour pressure over this solution is very low and the mist is not formed. The concentration of the acid in the absorbing tower slightly rises. Part of it is delivered for storage while the other part is reused in the process of irrigating the rings.

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1. What are the conditions for reversible exothermic reactions in industry?
2. What are the conditions for heterogeneous reactions?
3. What are the conditions for catalytic reactions?
4. How can the energy of exothermic reactions be utilized? Describe the design of the apparatuses.

11.8

Environmental Protection

The manufacture of sulphuric acid involves the processing and production of harmful substances such as hydrogen sulphide, sulphur(IV) oxide, sulphur(VI) oxide, and sulphuric acid. When present in air they have a harmful effect on man, animals, plants; they damage buildings (hydrogen sulphide forms explosive mixtures with air); the dust that is formed during crushing of materials containing sulphur is detrimental as well. Does this mean that chemical workers are exposed to danger? Several decades ago the workers engaged in the manufacture of sulphuric acid were indeed exposed to the harmful effects of these substances. The health of the workers deteriorated, and the harmful effects on buildings and the surrounding environment were also appreciable.

Now measures are taken to prevent pollution of the environment. The apparatuses are hermetically sealed; they are regularly inspected and properly maintained; the conditions for running the equipment are strictly observed; work shops are equipped with adequate ventilation; and devices designed to trap harmful substances from waste gases are used. Individual means of protection are also used in work shops where sulphuric acid is produced. Workers taking samples of the acid wear special goggles and gloves to protect their eyes and hands. Special gas masks are provided for emergency cases.

Much attention is given in the Soviet Union to protection of man and the environment, because industrial plants there are run for the good of all the people and not only for the profit of private owners.

? 1. Explain the flow diagram for the production of sulphuric acid shown in plate IV. Consider the flows of processed materials and heat; discuss the design of all process units and apparatuses; and characterize the conditions that are maintained in each process unit.

△ 2. Name the fields of use of sulphuric acid and describe the properties that account for its uses.

3. The annual outputs of sulphuric acid in the Soviet Union are as follows: 165 thousand tons in 1913; 5398 thousand tons in 1960; 8518 thousand tons in 1965; 12 058 thousand tons in 1970; and 22 400 thousand tons in 1978. Pre-revolutionary Russia only held 13th place in the list of major producers of sulphuric acid in the world. At the present time the Soviet Union is the world's second largest producer of sulphuric acid. What conclusion concerning the development of chemical industry can be drawn from these data?

I. Laboratory Exercises

1. Reaction of Zinc Hydroxide with Acids and Alkalis

Place a small amount of zinc hydroxide in a test tube and add hydrochloric acid; add a solution of sodium hydroxide to another portion of zinc hydroxide in another test tube. Stir the contents in the test tubes and observe. Can zinc hydroxide be classified as an acid or an a base?

2. Identification of Iodine by Starch. Identification of Hydrochloric Acid and Chlorides

Exercise 1. Fill a test tube the quarter full of dilute iodine water and add a few drops of starch solution. Observe the reaction.

Exercise 2. Fill a test tube one quarter full of a solution of potassium iodide and add a small portion of starch solution. Observe the reaction.

The colour of starch changes in Ex. 1 and remains unchanged in Ex. 2. Explain.

Exercise 3. Place hydrochloric acid in a test tube and add a few drops of silver nitrate. Write the reaction equation. Describe the appearance of silver chloride precipitate. What does it look like? Add 1 ml of nitric acid to the silver chloride precipitate. Does the acid dissolve the silver chloride?

Repeat the previous exercise but use sodium chloride instead of hydrochloric acid. Try to dissolve the precipitate with nitric acid.

Place 1 ml of sodium carbonate solution in a test tube and add a few drops of silver nitrate solution: silver carbonate precipitates. Add nitric acid to the precipitate. Does it dissolve silver carbonate?

Draw your own conclusion as to how hydrochloric acid and its salts can be identified?

3. Displacement of the Halogens by One Another from Their Compounds. Indentification of Bromides and Iodides

In order to establish which halogen can displace other halogens from their compounds, do as follows:

(1) test compounds of bromine and iodine with chlorine;
(2) test chlorine and iodine compounds with bromine;
(3) test chlorine and bromine compounds with iodine.

Exercise 1. Place solutions of potassium bromide and potassium iodide into separate test tubes. Add a small portion of chlorine water to both. Observe the reaction. Does chlorine displace bromine or iodine from their compounds?

Exercise 2. Place potassium chloride and potassium iodide solutions in separate test tubes and add bromine water to both solutions. Add 1-2 drops of starch solution to the test tube in which potassium iodide was placed. Observe the reaction. Does bromine displace chlorine or iodine from their compounds?

Exercise 3. Place potassium chloride and potassium bromide solutions in separate test tubes and add iodine water to both. Observe the reaction. Does iodine displace chlorine or bromine from their compounds?

Fill in the results of the exercises in the following table. Also write down equations for the reactions.

Halogen	Solutions		
Chlorine Bromine Iodine			

4. Examination of Specimens of Sulphur and Its Compounds

Thoroughly examine specimens of sulphur and its natural compounds and pay special attention to their states of aggregation in normal conditions, their colour, and odour.

Draw the table given below and fill in the results of your examinations.

Sample No.	Name	Composition (chemical formula)	Physical properties		
			state of aggregation	colour	odour

II. Practical Experiments

Experiment 1. Preparing Hydrochloric Acid. Experiments with Hydrochloric Acid

Hydrochloric acid is a solution of hydrogen chloride in water. Hydrogen chloride can be prepared by acting on a chloride (e.g. NaCl) with sulphuric acid. Write the reaction equation.

Preparing Hydrogen Chloride and Hydrochloric Acid

Assemble an apparatus as shown in Fig. II.7. Place sodium chloride in a flask (about 1/4 full) and carefully add sulphuric acid (2 : 1) so as only to wet the salt. Close the flask immediately with a stopper through which a gas-outlet tube is passed. Lower the gas-outlet tube into a test tube containing water (1/4 full), so that the end of the tube is 0.5 cm above the water surface. Heat the flask over a burner on a gauze with an asbestos centre. Observe the dissolution of hydrogen chloride in water in the test tube. An attentive eye will notice streaks of heavier liquid that move down from the water surface. Explain your observations. Pass hydrogen chloride into the water until the reaction in the flask stops. If the solution of hydrogen chloride in water warms up strongly, pass hydrogen chloride gas into another test tube containing cold water. Place the test tube containing the hydrochloric acid obtained in a stand. Keep it for future experiments.

Properties of Hydrochloric Acid

Divide the prepared acid into three equal portions (in three separate test tubes). Place a grain of zinc in one test tube and observe the reaction. Write down the reaction equation. Characterize the chemical properties of hydrochloric acid.

Experiment 2. Solving Problems for the Section 'The Halogens'

Problem 1. Prove experimentally that hydrochloric acid contains hydrogen and chlorine.

Problem 2. Establish whether a given sample of sodium nitrate contains chlorides.

Problem 3. Establish if the strip of paper given to you by the instructor is impregnated with starch and potassium iodide solution.

Problem 4. Prove experimentally that the substance given to you by the instructor is iodide.

Problem 5. Identify bromide in the substance given to you by the instructor.

Problem 6. Carry out the reactions specific for hydrochloric acid and sodium chloride.

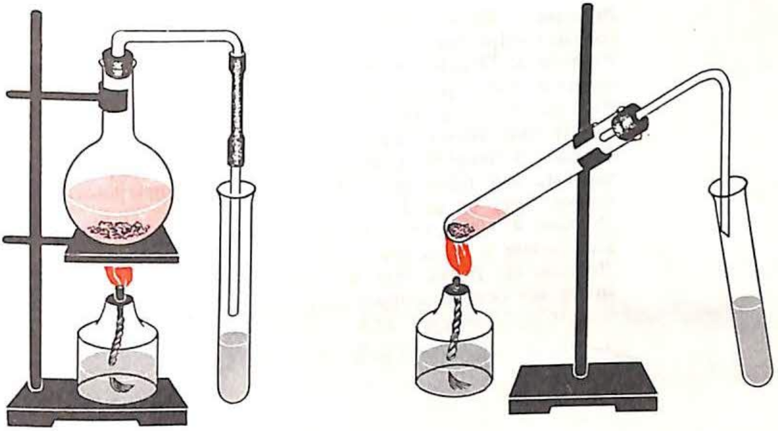


Fig. II.7 Apparatuses for obtaining hydrogen chloride and hydrochloric acid

Problem 7. Identify sodium chloride, sodium iodide, sodium bromide, and sodium carbonate which are given to you in four separate test tubes.

Problem 8. Half fill a test tube with bromine water, add zinc dust, stir with a glass rod, and heat slightly. Allow the liquid to settle. If the liquid is colourless transfer one half of the solution into another test tube. (If all the zinc has been used up in the reaction, but the solution remains coloured, add zinc, stir, and heat again.)

Add chlorine water to one test tube and silver nitrate solution to the other test tube. Observe the changes and explain them.

Problem 9. Identify hydrochloric acid, sodium hydroxide, and silver nitrate given to you in separate test tubes.

Experiment 3. Solving Problems for the Section 'Oxygen Subgroup'

Problem 1. Carry out reactions to test the qualitative composition of sulphuric acid.

Problem 2. Place 2-3 grains of zinc in two separate test tubes. Add about 1 ml of dilute sulphuric acid to one and concentrated sulphuric acid (*be careful*) to the other test tube. Observe the reaction. If no reaction occurs in either of the test tubes, heat slightly (*taking special precautions*). Observe the reaction. What is the reaction of zinc to dilute and concentrated sulphuric acid? Write reaction equations.

Problem 3. Pour sodium sulphide solution in two test tubes and add chlorine water to one, and bromine water to the other test tube. Observe the reactions and explain them.

Problem 4. Identify hydrochloric acid, sulphuric acid, and sodium hydroxide in three separate test tubes given to you by the instructor.

Problem 5. Prove that common salt contains (or does not contain) sulphates.

Problem 6. Decide whether a given salt is a sulphate, iodide, or chloride using specific reactions.

Problem 7. Using copper(II) oxide, prepare copper sulphate and isolate blue vitriol from it in the form of crystals.

Problem 8. Identify sulphate, sulphite, and sulphide in three separate test tubes given to you by the instructor. Only one reagent may be used.

Problem 9. Using an exchange reaction, prepare barium sulphate and isolate it from the mixture.

Problem 10. Prove that the blue crystals given to you by the instructor contain copper sulphate.

Answers to Questions Marked with an Asterisk:

page 126, 3.	Write the equation $x + 2O_2 = N_2 + 2CO_2$, whence $x = C_2N_2$.
page 149, 7.	The molecule of the given oxide cannot contain more than two oxygen atoms. If only one atom is contained, the atomic weight is 28 and the higher valency is 2, i.e. this element belongs to group II. The atomic weight of silicon is 28, but it stands in group IV. The element in question is therefore carbon.
page 162, 4.	Three bonds: one nonpolar covalent and two polar covalent bonds (between O and H).
page 168, 7.	$Xe^{8+}O_4^{2-}$, because the outer layer in the xenon atom is completed, and the electrons can only be displaced from xenon to oxygen.
page 183, 4.	Assume the capacity of the flask to be x litres. It will hold $x : 22.4$ mole HCl, which is $(35.5 + 1)x : 22.4$ g HCl. According to the result of the experiment, the same quantity is contained in the same volume of x litres in the form of hydrochloric acid. This means that 1 litre of the prepared hydrochloric acid contains $36.5 : 22.4 \doteq 1.64$ g HCl.
page 184, 5.	Silver chloride.
page 199, 2.	Sulphate, hydrogen sulphate.
page 200, 1.	Barium chloride.

Mendeleev's Periodic System

Periods	Series	GROUPS OF				
		I	II	III	IV	V
I	1	1 H Hydrogen 1.00797				
II	2	3 Li Lithium 6.939	4 Be Beryllium 9.012	5 B Boron 10.811	6 C Carbon 12.01115	7 N Nitrogen 14.007
III	3	11 Na Sodium 22.990	12 Mg Magnesium 24.312	13 Al Aluminium 26.982	14 Si Silicon 28,086	15 P Phosphorus 30.974
IV	4	19 K Potassium 39.102	20 Ca Calcium 40.08	Sc 21 Scandium 44.956	Ti 22 Titanium 47.90	V 23 Vanadium 50.942
	5	Cu 29 Copper 63.546	Zn 30 Zinc 65.37	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.922
V	6	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	Y 39 Yttrium 88.905	Zr 40 Zirconium 91.22	Nb 41 Niobium 92.906
	7	Ag 47 Silver 107.868	Cd 48 Cadmium 112.40	49 In Indium 114.82	50 Sn Tin 118.69	51 Sb Antimony 121.75
VI	8	55 Cs Cesium 132.905	56 Ba Barium 137.34	La* 57 Lanthanum 138.91	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.948
	9	Au 79 Gold 196.967	Hg 80 Mercury 200.59	81 Tl Thallium 204.37	82 Pb Lead 207.19	83 Bi Bismuth 208.980
VII	10	87 Fr Francium [223]	88 Ra Radium [226]	Ac** 89 Actinium [227]	Ku 104 Kurchatovium [264]	(Ns) 105 Nielsbohrium
Higher oxides		R_2O	RO	R_2O_3	RO_2	R_2O_5
Volatile hydrides					RH_4	RH_3

* Lanthanides	Ce 58 Cerium 140.12	Pr 59 Praseodymium 140.907	Nd 60 Neodymium 144.24	Pm 61 Promethium [145]	Sm 62 Samarium 150.35	Eu 63 Europium 151.96
** Actinides	Th 90 Thorium 232.038	Pa 91 Protactinium [231]	U 92 Uranium 238.03	Np 93 Neptunium [237]	Pu 94 Plutonium [242]	Am 95 Americium [243]

I. Mendeleev's periodic system of chemical elements

# of Chemical Elements

ELEMENTS					
VI	VII	VIII			
	(H)				2 He Helium 4.003
8 O Oxygen 15,9994	9 F Fluorine 18,998				10 Ne Neon 20.183
16 S Sulphur 32,064	17 Cl Chlorine 35,453				18 Ar Argon 39.948
Cr 24 Chromium 51.996	Mn 25 Manganese 54,938	Fe 26 Iron 55.847	Co 27 Cobalt 58,933	Ni 28 Nickel 58,71	
34 Se Selenium 78.96	35 Br Bromine 79,904				36 Kr Krypton 83,80
Mo 42 Molybdenum 95.94	Tc 43 Technetium [99]	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.905	Pd 46 Palladium 106.4	
52 Te Tellurium 127.60	53 I Iodine 126,904				54 Xe Xenon 131,30
W 74 Tungsten 183.85	Re 75 Rhenium 186.2	Os 76 Osmium 190,2	Ir 77 Iridium 192.2	Pt 78 Platinum 195.09	
84 Po Polonium [210]	85 At Astatine [210]				86 Rn Radon [222]
RO_3	R_2O_7	RO_4			
RH_2	RH				

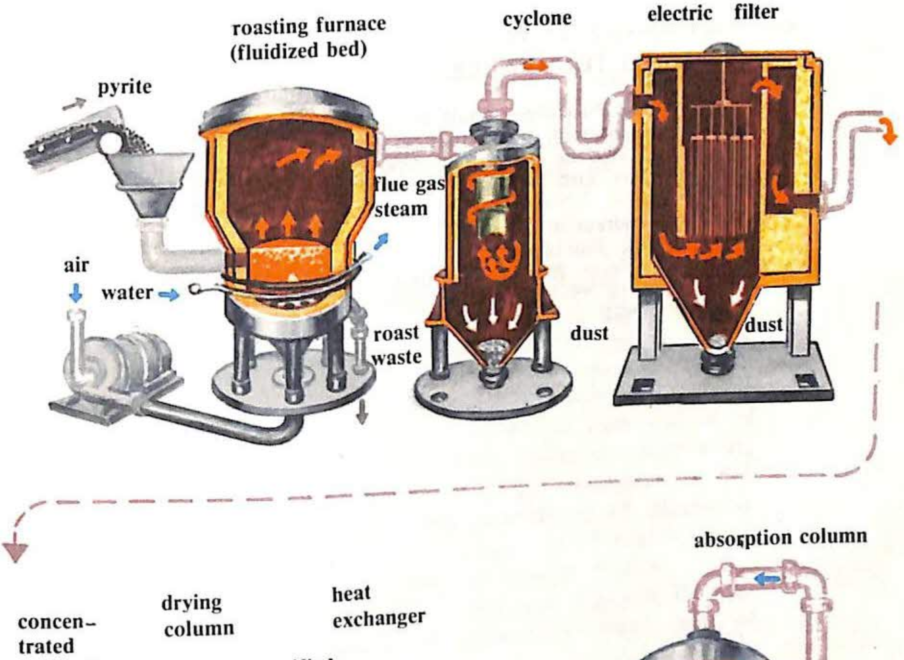
Gd 64 Gadolinium 157,25	Tb 65 Terbium 158,924	Dy 66 Dysprosium 162,50	Ho 67 Holmium 164,930	Er 68 Erbium 167,26	Tm 69 Thulium 168.934	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.97
Cm 96 Curium [247]	Bk 97 Berkelium [247]	Cf 98 Californium [249]	Es 99 Einsteinium [254]	Fm 100 Fermium [253]	Md 101 Mendelevium [256]	No 102 Nobelium [255]	Lr 103 Lawrencium [257]

Periods	Groups I	II	III	IV	V	VI	VII	VIII
I	1 H +1 1							2 He +2 2
II	3 Li +3 2 1	4 Be +4 2 2	5 B +5 2 3	6 C +6 2 4	7 N +7 2 5	8 O +8 2 6	9 F +9 2 7	10 Ne +10 2 8
III	11 Na +11 2 8 1	12 Mg +12 2 8 2	13 Al +13 2 8 3	14 Si +14 2 8 4	15 P +15 2 8 5	16 S +16 2 8 6	17 Cl +17 2 8 7	18 Ar +18 2 8 8

II. Distribution of electrons by layers in atoms of the elements of short periods

Periods	Groups I	II	III	IV	V	VI	VII	VIII		
III	11 Na +11 2 8 1	12 Mg +12 2 8 2	13 Al +13 2 8 3	14 Si +14 2 8 4	15 P +15 2 8 5	16 S +16 2 8 6	17 Cl +17 2 8 7			18 Ar +18 2 8 8
IV	19 K +19 2 8 8 1	20 Ca +20 2 8 8 2	Sc 21 +21 2 9 8 2	Ti 22 +22 2 10 8 2	V 23 +23 2 11 8 2	Cr 24 +24 1 13 8 2	Mn 25 +25 2 13 8 2	Fe 26 +26 2 14 8 2	Co 27 +27 2 15 8 2	Ni 28 +28 2 16 8 2
	Cu 29 +29 1 18 8 2	Zn 30 +30 2 18 8 2	31 Ga +31 2 8 18 3	32 Ge +32 2 8 18 4	33 As +33 2 8 18 5	34 Se +34 2 8 18 6	35 Br +35 2 8 18 7			36 Kr +36 2 8 18 8

III. Distribution of electrons by layers in atoms of the elements of short (III) and long (IV) periods



IV. Manufacture of sulphuric acid

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